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PRECIPITATION CHEMISTRY

PRECIPITATION CHEMISTRY

I. PRECIPITATION ACIDITY MEASUREMENTS

II. SPECIFIC CONDUCTANCE AND ION CONCENTRATIONS

by

Yan K. Lau

Air Quality Control Branch
Pollution Control Division
Alberta Environment

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ABSTRACT

The chemical aspects of acidity measurements on precipitation samples are discussed in the first part of the report. The three methods for measuring precipitation acidity are studied. They are pH measurement, titration and cation-anion balance. Theoretical correlations between different measurement methods are derived. The correlation between pH measurement and cation-anion balance is tested by actual data. It holds for acidic precipitation but it breaks down for basic precipitation. The different methods for averaging precipitation acidity are investigated. The weighted hydrogen ion concentration average is the preferred method. But to compare precipitation acidity measured on an event basis with that measured on a bulk basis, the use of the weighted "effective $[H^+]$" ($[H^+] - [HCO_3^-]$) average is required. The effects of temperature on the acidic contribution by atmospheric CO_2 and SO_2 are studied. The effects are expected to be more significant with SO_2 than with CO_2.

In the second part of the report, the possibility of using specific conductance - ion concentration correlation as a quality assurance index for chemical analyses of precipitation samples is investigated. A theoretical expression is derived and it is supported by actual data. The correlation shows that the 1977 - 1978 Alberta precipitation data are of acceptable quality.

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PRECIPITATION CHEMISTRY

I. PRECIPITATION ACIDITY MEASUREMENTS

PRECIPITATION CHEMISTRY

I. PRECIPITATION ACIDITY MEASUREMENTS

1. Background

The objective of this study is to analyze the different methods used for measuring precipitation acidity. It is hoped that better understanding in the interpretation and the correlation of results would allow one to set up a data quality assurance program on precipitation acidity measurements.

The acidity of water is a measure of its capacity to donate protons, H^+. Acidity may be expressed quantitatively as concentration per unit volume (e.g. mole litre^{-1}) of hydrogen ions (protons) or as pH values. pH is defined as $-\log A_{H+}$ where A_{H+} is the activity of the hydrogen ion. In the case of precipitation which is approximately an infinitely dilute solution, it is correct to say that pH = $-\log [H^+]$ where $[H^+]$ is the concentration of hydrogen ion in unit of mole litre^{-1}.

Neutral water has a pH of 7. This is because the ionization product of water at 25°C is 10^{-14}mole^{2}l^{-2}. Charge neutrality

$$[H^+]\ [OH^-] = 10^{-14} \qquad (1.1)$$

requires that $[H^+] = [OH^-]$. Therefore, it leads to the result that the concentration of hydrogen ion is 10^{-7} mole l^{-1}.

Normal precipitation has a pH value different from 7. This is because of the presence of atmospheric CO_2 which is in equilibrium with the precipitation according to the following reaction:

$$CO_2 + H_2O = H^+ + HCO_3^- \qquad (1.2)$$

At 25°C, reaction 1.2 has an equilibrium expression (Reuss 1975):

$$\frac{[H^+]\ [HCO_3^-]}{[CO_2]_g} = 10^{-7.81} \qquad (1.3)$$

With standard atmospheric CO_2 concentration of 316 ppm (3.16×10^{-4} atmosphere), equation 1.4 is obtained.

$$[H^+]\ [HCO_3^-] = 10^{-11.31} \qquad (1.4)$$

Again, charge neutrality requires $[H^+] = [HCO_3^-] = 10^{-5.65}$ mole l^{-1}. Therefore, pure precipitation at 25°C in equilibrium with atmospheric CO_2 is expected to have a pH value of 5.65. The significance of the results is that the concentration of H^+ and HCO_3^- is inter-related by reaction 1.2. When the precipitation or soil solution is more acidic than pH 5.65 (lower pH value) due to the presence of unnatural components, the concentration of HCO_3^- will decrease proportionally according to the constraint set by equation 1.4. The common cause of acidic precipitation (acid rain) is the emission of sulphur dioxide and nitrogen oxides to the atmosphere.

SO_2 and NO_x upon oxidation and hydration in the atmosphere produce sulphuric acid and nitric acid respectively.

The presence of HCO_3^- in precipitation also has an important bearing on its alkalinity which is a measure of its capacity to accept protons. When precipitation is in equilibrium with atmospheric CO_2, equation 1.3 applies.

$$\frac{[H^+]\ [HCO_3^-]}{[CO_2]_g} = 10^{-7.81} \qquad (1.3)$$

By substituting the relationship $[H^+] = \frac{10^{-14}}{[OH^-]}$ into equation 1.3, an interesting expressic.. (equation 1.5) which is the equilibrium expression for

$$\frac{[HCO_3^-]}{[CO_2]\ [OH^-]} = 10^{6.19} \qquad (1.5)$$

reaction 1.6 is obtained. With atmospheric CO_2 concentration of

$$CO_2 + OH^- = HCO_3^- \qquad (1.6)$$

3.16×10^{-4}, equation 1.5 becomes:

$$\frac{[HCO_3^-]}{[OH^-]} = 490 \qquad (1.7)$$

The significance of expression 1.7 is that the concentration of the much less basic anion HCO_3^- will be 490 times that of the very basic anion OH^- as long as the precipitation is in equilibrium with standard atmospheric CO_2. Therefore, even though hydroxides may be formed by the hydration of alkaline oxides (e.g. Na_2O) and alkaline earth oxides (e.g. CaO) in the atmosphere from the burning of fuel high in the corresponding cations, most

of the OH^- would be converted to HCO_3^- in precipitation, keeping it from becoming excessively alkaline. The presence of bicarbonate ion thus acts as an effective buffer to prevent highly alkaline conditions from occurring in rainwater. This accounts for the absence of a "basic rain" problem.

2. Method for Precipitation Acidity Measurements

Three methods are commonly used to measure precipitation acidity. They are: (a) pH measurement, (b) titration, and (c) cation-anion balance. Although their common objective is to measure proton (hydrogen ion) concentration the types of protons which an individual method can measure differ. Methods (a) and (c) will measure free protons (mostly associated with strong acids such as H_2SO_4 or HNO_3). The former is a direct measurement of free protons while the latter measures proton concentration in an indirect way. Method (b) is a more flexible method. It will measure free protons together with some bound protons (associated with weak acids such as NH_4^+). The extent of weak acids that it will measure depends on the endpoint pH chosen for the titration. Care has to be taken when comparing acidity results obtained from different methods.

2.1 pH Measurement

The simplest method to measure precipitation acidity is the pH measurement. A pH meter which is a combination of a glass electrode and a standard reference electrode is used for the measurement. The pH value,

which is the negative of the common logarithm of hydrogen ion activity (concentration), is read directly from the meter. The hydrogen ion concentration may be calculated from the equation $[H^+] = 10^{-pH}$.

The pH measurement will only measure the concentration of the free hydrogen ions. Strong acids such as H_2SO_4 or HNO_3 ionize completely to give H^+ under normal measurement conditions. Their contribution to the precipitation acidity is thus completely accounted for by this method. The contribution of weak acids such as the ammonium ion NH_4^+, toward precipitation acidity will depend on the pH of the sample. In the case of NH_4^+, equilibrium 1.8 should be considered. From the equilibrium constant shown in equation 1.9,

$$NH_4^+ = H^+ + NH_3 \qquad (1.8)$$

at 25°C

$$\frac{[H^+]\,[NH_3]}{[NH_4^+]} = 5.6 \times 10^{-10} \qquad (1.9)$$

it may be calculated that at pH 5.65, $[NH_3]/[NH_4^+] = 2.5 \times 10^{-4}$. That is, more than 99.9% of the ammonium ion will remain as NH_4^+ (bound protons) and its acidity will not be "seen" by the pH electrodes (Tyre 1981). But if the aqueous solution is at pH 9, $[NH_3]/[NH_4^+] = 0.56$ Approximately 36% of the ammonium ions would be converted to ammonia and free protons. A partial contribution to acidity by the weak acid NH_4^+ will be observed in this case. From the above discussion, it is concluded that pH measurement should give a good measure of the contribution of SO_2 and NO_x to the acidity of precipitation. Weak acid contribution is often undetected.

A major problem associated with precipitation acidity measurements is the presence of the CO_2 - H_2O equilibrium 1.2.

$$CO_2 + H_2O = H^+ + HCO_3^- \qquad (1.2)$$

The presence of the equilibrium results in the fact that the concentration of H^+ will vary with the partial pressure of CO_2 which is in equilibrium with the precipitation sample. The effect of CO_2 partial pressure on pH ($= -\log [H^+]$) value is illustrated in Figure 1.1 (Reuss 1975). The dotted line indicates the standard atmospheric CO_2 pressure (316 ppm) and the numbers refer to pH at 316 ppm. It can be seen from Figure 1.1 that for pH >5, pH value decreases with increasing CO_2 partial pressure. The variation of the equilibrium CO_2 partial pressure has to be considered when the accuracy and precision of pH measurements are examined. For example, normal rainwater will have pH 5.65 when it is in equilibrium with 316 ppm CO_2. If the CO_2 concentration is increased to 500 ppm, the resulting pH will be 5.55. The effect of CO_2 variation will be larger at higher pH values. Thus, in order to obtain consistent and reproducible results, pH measurement should be performed under a known standard CO_2 partial pressure (e.g. 316 ppm). If this is not possible, time should be allowed for precipitation samples to establish equilibrium with the CO_2 partial pressure in the laboratory environment which is less likely to have a large variation with time.

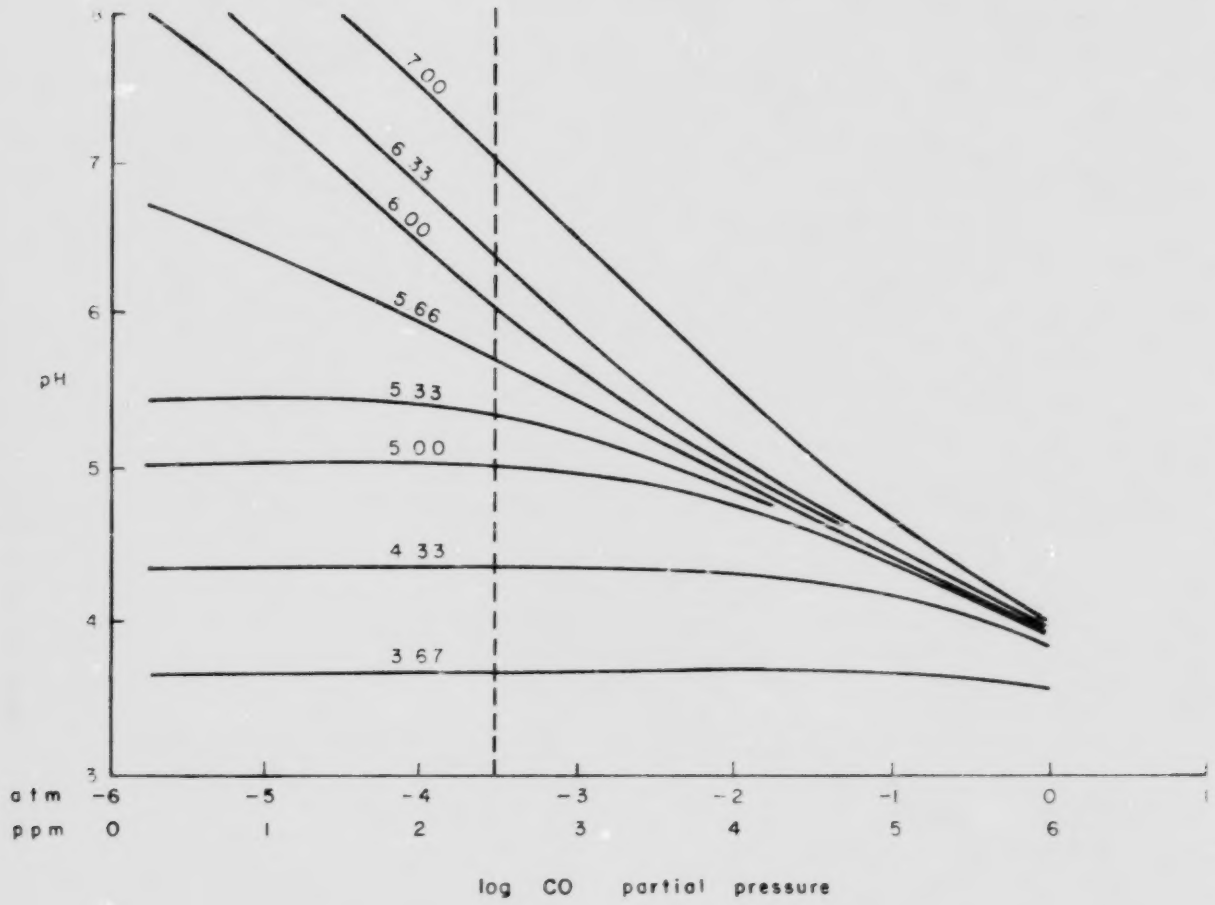

FIGURE 1.1 EFFECTS OF CO_2 PARTIAL PRESSURE ON pH. DOTTED LINE INDICATES 316 ppm CO_2 AND NUMBERS REFER TO pH AT 316 ppm CO_2 (REUSS 1975)

2.2 Titrimetric Method

The titrimetric procedures for precipitation acidity measurement vary from laboratory to laboratory. The major difference among various procedures is the endpoint selected for titration. For example, the World Meteorological Organization (1976) recommended an endpoint of pH 5.6; the American Public Health Association (1980) recommended an endpoint of pH = 8.3 and Galloway et al. (1976) suggested titration to pH = 9.0. The acidity measurements by titration include all free protons that would be present at the endpoint pH. In other words, the higher the endpoint pH, the larger is the portion of weak acids that are accounted for. Therefore, for "total acidity" measurement, it is desirable to select an endpoint of pH 8-9. But for measuring the contribution of SO_2 and NO_x to total acidity of precipitation, it is better to select an endpoint of pH 5.6 (pH of "neutral" rainwater).

The titrimetric procedure adopted by Alberta Environment (endpoint pH = 5.6) is described below. The principle is to determine the concentration of H^+ in the absence of the CO_2 - [illegible] equilibrium 1.2. The procedure involves the following steps:

$$CO_2 + H_2O = H^+ + HCO_3^- \qquad (1.2)$$

(a) the addition of a measured amount of a standard sulphuric acid to the precipitation sample, to pH 4; if the sample has a pH <4, no acid addition is necessary;

(b) the purging of samples with nitrogen gas to remove carbon dioxide formed from the bicarbonate ions;

(c) back titration under nitrogen atmosphere with standard sodium hydroxide solution to pH 5.6. The amount of hydrogen ions present in a known volume is obtained by subtracting the amount of sulphuric acid used from that of sodium hdyroxide consumed in back-titration

The method described gives a better representation of all available H^+ in precipitation for long-term H^+ loading in soil. It is a measure of excessive H^+ concentration (over natural acidity) minus HCO_3^- concentration (alkaline portion of precipitation). Since the CO_2 - H_2O equlibrium is no longer present in the system, the CO_2 partial pressure does not have an effect on the measurement.

The results from pH measurement and titration may be compared if the endpoint of titration is specified. The expected agreement is illustrated by the following calculation. Rainwater having pH 5 at 316 ppm CO_2 partial pressure is used as an example. (All H^+ are assumed to be from strong acids.)

Titration (endpoint at pH 5.6)

precipitation sample: 1 litre

$$CO_2 + H_2O = H^+ + HCO_3^-$$

pH = 5

↓ H^+ required = $9 \times 10^{-5} + 4.90 \times 10^{-7}$ = 9.05×10^{-5} mole

pH = 4

↓ OH^- required = 9.75×10^{-5} mole

pH = 5.6

10^{-5} mole ↓ 10^{-4} mole ↓ $10^{5.6}$ mole

4.9×10^{-7} mole ↓ (removed as CO_2) ↓ nil

$$\text{ACIDITY BY TITRATION} = 9.75 \times 10^{-5} - 9.05 \times 10^{-5}$$
$$= 7.0 \times 10^{-6} \text{ mole } l^{-1}$$

pH Measurement

Acidity in excess of normal precipitation, $[\text{Acidity}]_{pH}$

$$= 10^{-5} - 10^{-5.6}$$
$$= 7.49 \times 10^{-6} \text{ mole } l^{-1}$$

$$[\text{Acidity}]_{pH} - [HCO_3^-] = [\text{Acidity}]_{\text{titration}}$$

Since the concentration of HCO_3^- can be calculated by equation 1.3 if $[H^+]$ and $[CO_2]$ are known, acidity measurements by both methods can be compared. Good agreement is expected if the acidic contribution is not pH dependent.

Besides using a fixed endpoint pH, the acidity of a precipitation sample can be measured by titration with NaOH using Gran's plot (Gran 1952, Askne et al. 1972). The method consists of plotting the function, $\psi = (V_o + V)\ 10^{(E-Eo)/(RT/nF)}$, versus V, where

V_o = sample volume

V = volume of base added

E = emf-values corresponding to V

Eo = emf-value corresponding to Vo

$\frac{RT}{nF}$ = 59.157 mV at 25°C

A linear relation is expected for strong acids. In that case, when $\psi = 0$, V = Ve; where Ve is the equivalent volume of base required to

neutralize the acids. If weak acids are present, deviation from linearity will occur when approaching the point of equivalence. This is because the acidic contributions by weak acids are always pH dependent, especially near the point of equivalence. However, strong acidity can be determined by extrapolation of the linear portion of the Gran's plot.

Strong acidity and weak acidity can be measured at the same time if the Gran's plot is examined past the point of equivalence (Gran 1952; Krupa et al. 1976; Kluckner et al. 1980). Instead of plotting ψ versus V, the function $\Psi = (Vo + V) \times 10^{'E'/59.157}$ is plotted against V, where 'E' is the absolute emf-value corresponding to V. Since Eo is constant for a given sample, $\Psi = 0$ when $\psi = 0$. On the acidic side of the titration curve, the extrapolated intercept ($\Psi = 0$) of the linear portion of the plot, $\Psi = (Vo + V) \times 10^{+E/59.157}$ versus V, yields equivalent base volume for calculating strong acidity. On the basic side of the titration plot of $\Psi = (Vo + V) \times 10^{-E/59.157}$ versus V, the extrapolated intercept ($\Psi = 0$) should be equal to the equivalent volume of base required to neutralize all acidic components, strong and weak acids included.

The set of titration data shown in Table 1.1 illustrates the determination of acidity by Gran's plot. The corresponding Gran's plot is shown in Figure 1.2. The treatment of data is very straightforward. From the plot in Figure 1.2, the strong acidity in the sample = 19.8×10^{-6} mole/litre (corresponding to pH 4.7), total acidity = 35.5×10^{-6} mole/litre (pH 4.5). Hence weak acidity = $35.5 \times 10^{-6} - 19.8 \times 10^{-6} = 15.7 \times 10^{-6}$ mole/litre. The expected pH of the sample by direct measurement should be between 4.7 and 4.5, and it will probably be closer to the former than to the latter.

TABLE 1.1

ACIDITY DETERMINATION BY TITRATION (GRAN'S PLOT)

Vo (ml)	V (ml)	E (mV)	Vo + V (ml)	Ψ/1000 (ml)
40	0	116	40.00	3.66
	0.01	113	40.01	2.25
	0.02	109	40.02	2.79
	0.03	104	40.03	2.29
	0.04	98	40.04	1.82
	0.05	91	40.05	1.38
	0.06	84	40.06	1.05
	0.07	75	40.07	0.74
	0.08	66	40.08	0.52
	0.09	56	40.09	0.36
	0.18	-88	40.18	1.23
	0.20	-100	40.20	1.97
	0.22	-107	40.22	2.59
	0.24	-113	40.24	3.27
	0.26	-118	40.26	3.98
	0.28	-122	40.28	4.65
	0.30	-125	40.30	5.23

$\Psi = (Vo + V) \times 10^{|E|/(RT/nF)}$

where Vo = sample volume; V = titrant volume

$|E|$ = absolute mV reading; $\frac{(RT)}{(nF)}$ = 59.157 mV at 25°C

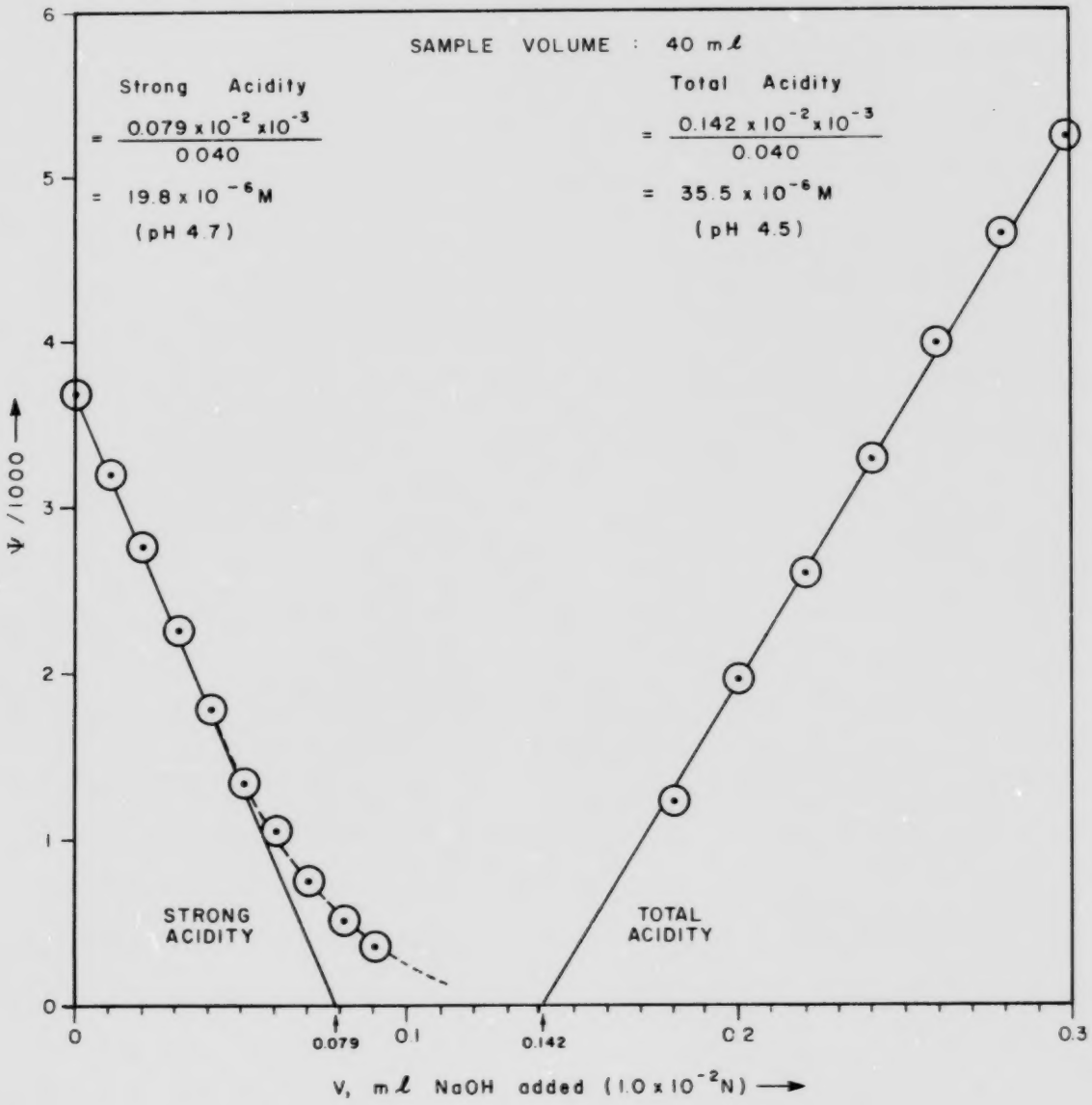

FIGURE 1.2 ACIDITY DETERMINATION BY GRAN'S PLOT

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On the whole, titration method of using Gran's plot should be preferred over other titration procedures. It does not only provide uniform definition on strong acidity and weak acidity, but allows the determination of both. The more tedious procedure involved can be overcome with the aid of some automation of equipment.

The titration should be carried out under an inert (N_2) atmosphere in the absence of any further CO_2 effects. This can be achieved easily by using a closed jacket-beaker. The presence of CO_2 does not have any effect on the determination of strong acidity. But its effects on weak acidity (or total acidity if little strong acid is present) would be significant. The solubility of CO_2 in H_2O increases rapidly when pH>5 (e.g. 20 μeq/litre at pH 5 and 5,000 μeq/litre at pH 9). Since the carbonic acid will be measured as a weak acid, the results would reflect exchange rates of CO_2 between atmosphere and H_2O as influenced by operational parameters such as stirring. (Note. stirring is necessary for thorough mixing which is essential for titration, yet it speeds up exchange rates of CO_2 in the system). If titration is not performed under an N_2 atmosphere, higher total acidity and questionable reproducibility would result. This is critical where precipitation is not strongly acidic and/or only total acidity determination is practicable. Most precipitation in Alberta fits this description.

In cases where complete elimination of CO_2 - H_2O equilibrium is desired, titration should be done under an N_2 atmosphere after thorough nitrogen purging, a common procedure used to displace CO_2 from the system.

The back-titration technique as described previously may also be adapted to the Gran's plot method for this purpose.

In summary, the suggested procedure for performing titration using Gran's plot is presented below:

(a) Place a known volume (e.g. 40 ml) of sample under N_2 atmosphere and record initial mV reading from a calibrated pH meter.

(b) Stir the sample slowly; add a small increment (e.g. 10 µl) of NaOH (e.g. 10^{-2}N) at a time; record mV readings after equilibrium (e.g. 20 s).

(c) Take 4 to 5 readings on the acidic side (+mV), then add enough NaOH to shift the system to the basic side (-mV).

(d) Take 4 or 5 readings on the basic side at small increments (e.g. 20 µl) of the NaOH solution.

(e) Construct a Gran's plot by plotting Ψ versus V as in Figure 1.2.

(f) Strong acidity and total acidity are calculated from the appropriate equivalent base volumes, Ve.

$$\text{Acidity (mole/litre)} = \frac{\text{Ve(ml)} \times \text{N (mole/litre)} \times 10^{-3}\ \text{l/ml}}{\text{V (litre)}}$$

where N = normality or molarity of NaOH

V = volume of sample used

2.3 Cation - Anion Balance

A solution has to maintain its electrical neutrality. By balancing cations and anions in a solution quantitatively, any charge discrepancy in favor of anions may be assumed to be made up by hydrogen ions. This method will only measure free protons, that is, strong acids that dissociate completely in aqueous media under normal conditions. Major cations commonly encountered in precipitation are Ca^{2+} Mg^{2+} Na^{+}, K^{+} and NH_4^{+}. Major anions in the system are NO_3^{-}, Cl^{-} and SO_4^{2-}. The bicarbonate anion, HCO_3^{-}, is normally not included in the calculation because its concentration is in equilibrium with atmospheric CO_2 according to reaction 1.2. The

$$CO_2 + H_2O = H^+ + HCO_3^- \qquad (1.2)$$

relationship between pH and HCO_3^{-} concentration in equilibrium with atmospheric CO_2 (316 ppm) is illustrated in Figure 1.3 (Reuss 1975). It can be seen that the concentration of HCO_3^{-} at pH<5 is insignificant. But HCO_3^{-} concentration increases very rapidly at higher pH, making a sizable contribution toward the total ionic concentration. In order to measure consistently the acidity contribution from sources other than CO_2, the HCO_3^{-} anion is excluded from the cation - anion balance. This is equivalent to removing the CO_2 - H_2O equilibrium from the system, a condition frequently used in the titration method.

The "metallic" cations (all except NH_4^{+}) may be analyzed with an atomic absorption spectrophotometer, either in flame absorption mode or in

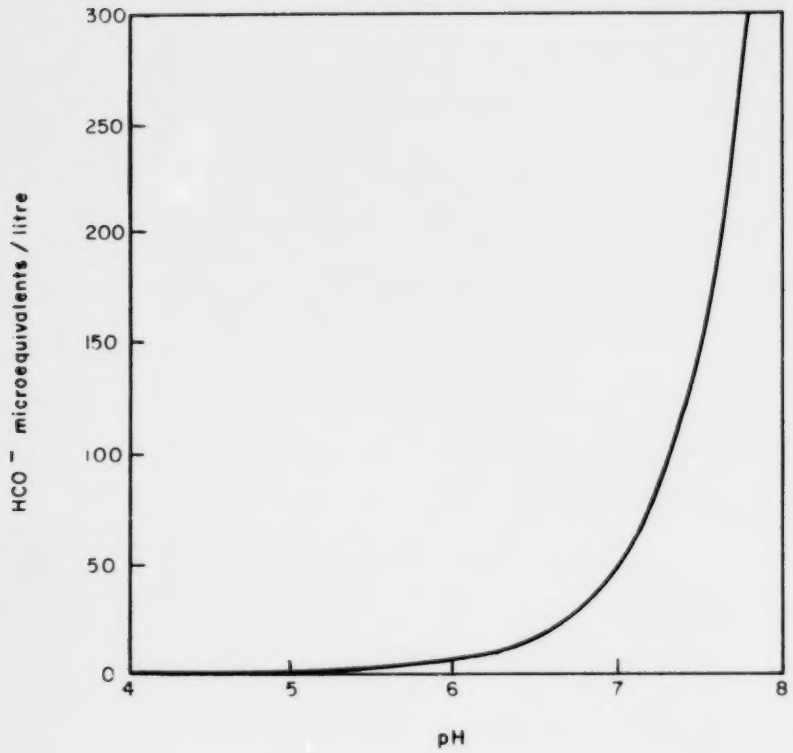

FIGURE 1.3 pH DEPENDENCE OF HCO_3^- CONCENTRATION OF PRECIPITATION IN EQUILIBRIUM WITH 316 ppm CO_2 (REUSS 1975)

flame emission mode. NH_4^+ and the anions may be analyzed colorimetrically. Alternately, cations and anions may be analyzed by ion chromatography. If the concentration is expressed in moles per litre (mole is equal to weight divided by its molecular weight), the acidity may be expressed as follows:

$$\text{ACIDITY} = [NO_3^-] + [Cl^-] + 2[SO_4^{2-}] - 2[Ca^{2+}] - 2[Mg^{2+}] - [Na^+] - [K^+] - [NH_4^+] \qquad (1.10)$$

The acidity measured is the concentration of H^+ minus HCO_3^- in mole l^{-1}. A factor of 2 appears with doubly charged species in the above expression. This is because cations and anions have to be balanced on an equivalent basis so that electrical neutrality results.

Since both the titrimetric method and the anion minus cation method exclude the effects of the CO_2 - H_2O equilibrium system, their results should be comparable. But the endpoint pH chosen for titration has to be taken into consideration if direct comparison is to be made. Also, results from pH measurement can be compared with those from cation - anion balance. Both methods will measure only free protons. The relationship is:

$$\text{total } [H^+] - [HCO_3^-] = \text{Anions - Cations (excludes } HCO_3^-)$$
$$\text{or } 10^{-pH} - [HCO_3^-] = \text{Anions - Cations (excludes } HCO_3^-) \qquad (1.11)$$

Assuming pH measurement is performed under atmospheric CO_2 partial pressure, $[HCO_3^-]$ at any pH may be calculated.

The method of cation - anion balance should only be used as a measure of acidity for precipitation at or below pH 5.6 (i.e. more acidic than normal precipitation). When precipitation is less acidic than normal (pH 5.6), the HCO_3^- ions may be considered as the alkaline component of the precipitation as $[HCO_3^-]$ will be 490 times higher than $[OH^-]$ according to equation 1.7. Therefore, the quantity which will be measured is the concentration of HCO_3^- ions in excess of H^+ ions. Since the proton affinity of HCO_3^- in aqueous media is much less than that of OH^- ions the cation - anion balance method will not measure acidity directly when the precipitation is alkaline. However, the correlation 1.11 is still expected to hold. The balance of negative values

$$10^{-pH} - [HCO_3^-] = \text{Anions} - \text{Cations (excludes } HCO_3^-) \quad (1.11)$$

on both sides of equation 1.11 is then a balance of HCO_3^- ions. The correlation 1.11 would fail only when ions not included in the analysis start to contribute significantly. For example, if the precipitation is very alkaline (pH>9), the contribution of CO_3^{2-} from HCO_3^- to the anion concentration will become significant. Another pitfall of the method is that the acidity measured would often be a relatively small difference between two large numbers. This is especially the case when the pH of precipitation is about 5.6. It is expected that both the accuracy and the precision of the measurement would decrease as the acidity expressed in H^+ mole l^{-1} is getting small relative to the total ion concentration which is in the order of $10^1 - 10^2$ μmole l^{-1} for normal precipitation.

To compare results of acidity measurements by pH methods and cation - anion balance, 28 data sets were chosen from the Alberta Environment Precipitation Quality Data Summary from April 1978 to December 1979. Completeness in cation - anion analyses is the criterion used in choosing the data sets. All data with pH<5 during the period were included. The HCO_3^- ion concentrations were calculated by assuming that precipitation samples were in equilibrium with standard atmospheric CO_2 partial pressure of 316 ppm at 25°C. The results from pH measurements are expressed in terms of $10^{-pH} - [HCO_3^-]$. The results from cation - anion balance are expressed as anions minus cations on an equivalent basis (equation 1.10). Both are in units of μmole l^{-1}. The data sets are tabulated in Table 1.2. Their correlations are illustrated in Figure 1.4. According to equation 1.11, a 1:1 correlation should be expected. It is clear from Figure 1.4 that the correlations between results from the two acidity measurement methods are not what an experimental scientist would consider adequate. If only precipitation at or below pH 5.6 (top right quadrant of Figure 1.4) are considered, the trend of 1:1 correlations is visible provided that the "outliers" are ignored. No 1:1 correlation is observed for precipitation with pH>5.6. It is interesting to note that the bulk of scattering appears to arise from the negative values (basic precipitation). Whether this reflects analytical errors or wrong assumptions in modelling is not known. There may be anions (e.g. metal - complex anions such as $Al[OH]_4^-$) which are not analyzed but are present in significant quantities when the precipitation is basic. At this point, no speculation should be made until results from further studies are available. But it is fair to conclude that the 1:1 correlation between "$[H^+] - [HCO_3^-]$" and "cations minus

TABLE 1.2

ACIDITY (μmole l^{-1}) FROM ALBERTA PRECIPITATION QUALITY DATA

(I) Alberta Environment Stations

*	pH Method $[H^+] - [HCO_3^-]$	Cation - Anion Balance	
		Normal Balance	Removal of Marine Contribution
(12)	50	34	35
(11)	15.6	10	-140
(14)	12.2	43	52
(15)	12.2	42	42
(8)	12.2	5.4	7.0
(9)	7.3	82	6.3
(7)	-0.45	-20	-18
(4)	-3.9	2.2	4.8
(5)	-7.1	8.0	12
(3)	-11.9	-230	-227
(2)	-49	30	25
(10)	-49	-218	-222
(6)	-93.3	-2.7	5.7
(1)	-98	15	8.9
(13)	-155	-306	-301

* Site number. For site documentation, see Appendix I of the report.

TABLE 1.2 (continued)

(II) Federal Government Stations

*	pH Method $[H^+] - [HCO_3^-]$	Cation - Anion Balance	
		Normal Balance	Removal of Marine Contribution
(25)	12.2	18	23
(27)	9.5	28	24
(26)	2.8	-6.2	1.1
(20)	-3.9	-3.0	6.4
(23)	-3.9	-28	-32
(19)	-5.4	-30	-0.79
(18)	-7.1	-24	-27
(17)	-7.1	-93	-73
(16)	-15.2	-158	-158
(21)	-24	-170	-162
(28)	-31	-254	-204
(24)	-39	-40	-41
(22)	-49	-310	-318

* Site number. For site documentation, see Appendix I of the report.

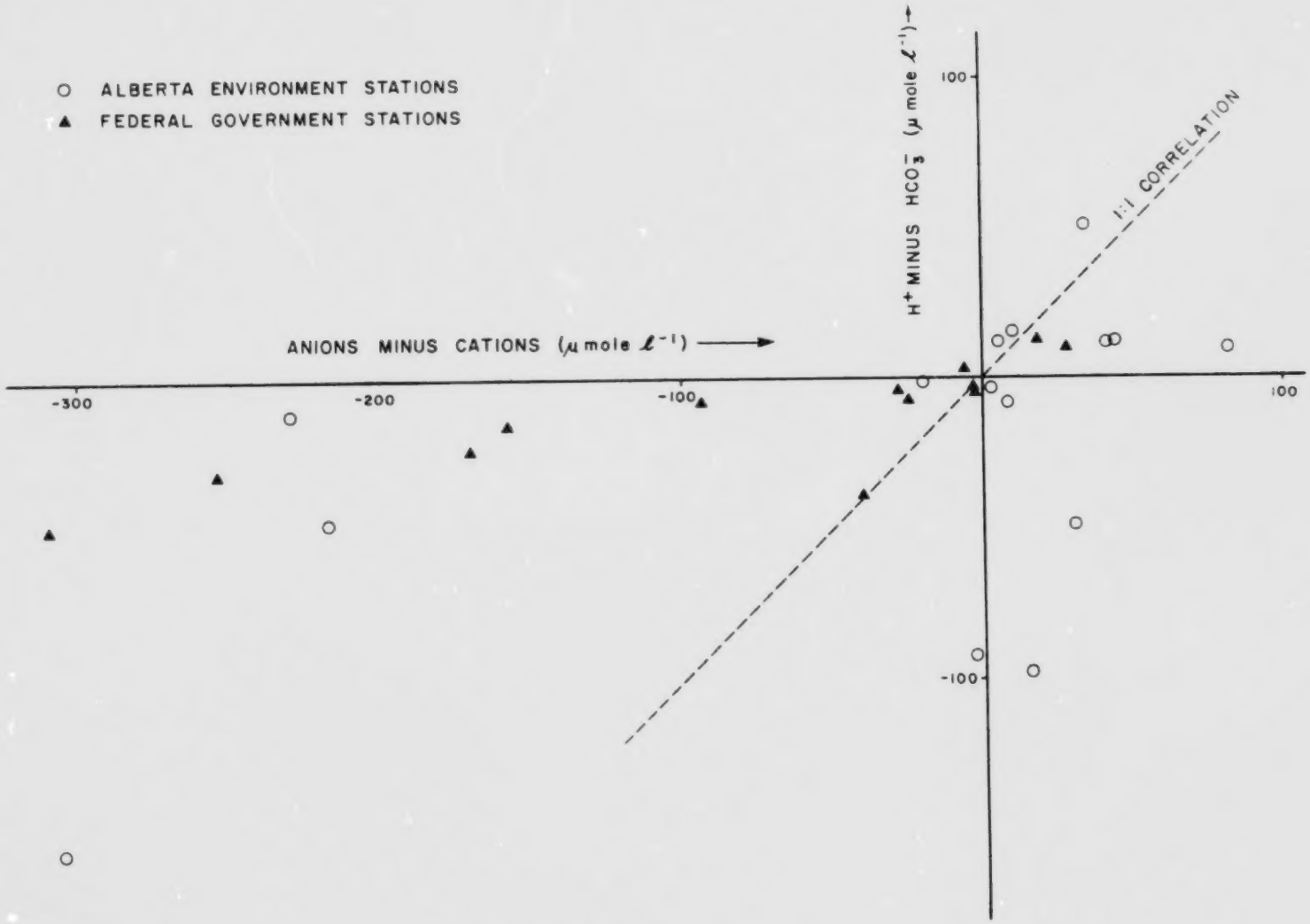

FIGURE 1.4 CORRELATION BETWEEN "H^+ MINUS HCO_3^-" AND "ANIONS MINUS CATIONS"

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anions" should hold for acidic precipitation. It provides a useful check on acidity measurement especially when the precipitation is considerably acidic (pH<5). Larger scattering in such correlation is expected when the acidity of precipitation is toward "normal" (pH 5.6) due to inherent errors in numerical analysis. The correlation does not seem to hold for negative values (basic precipitation) which are a measure of HCO_3^- concentration instead of H^+ concentration.

The method of cation - anion balance can be modified to take into account contributions of marine origin. The model suggested by Granet (1972) is based on the assumption that all sodium ions and chloride ions are of marine origin. The fraction of the SO_4^{2-}, Ca^{2+} Mg^{2+}, and K^+ assumed to be of marine origin is equal to the concentration of Na^+ times the ratio of the respective ion in sea water to the concentration of Na^+ in sea water. The resulting expression is shown below:

$$\text{Acidity} = [NO_3^-] + 2([SO_4^{2-}] - \frac{27.6}{457}[Na^+])$$
$$- 2([Ca^{2+}] - \frac{10.0}{457}[Na^+]) - 2([Mg^{2+}] - \frac{111.2}{457}[Na^+])$$
$$- ([K^+] - \frac{9.7}{457}[Na^+]) - [NH_4^+]$$

The above expression may be simplified to give:

$$\text{Acidity} = [NO_3^-] + 2[SO_4^{2-}]$$
$$- 2[Ca^{2+}] - 2[Mg^{2+}] - [K^+] - [NH_4^+]$$
$$+ 0.19[Na^+] \qquad (1.12)$$

This is equivalent to the previous equation 1.10 for cation - anion balance if the molar ratio of Cl^- to Na^+ in the rainfall is 1.19, the ratio found in sea water.

The same 28 data sets used in Figure 1.4 are employed for calculating acidity using equation 1.12. The results are also tabulated in Table 1.2. The correlation of H^+ minus HCO_3^- and anions minus cations (minus contributions from sea salts) is shown in Figure 1.5. It can be seen that there is no noticeable difference in correlation from that in Figure 1.4. It may be concluded that marine effects on the acidity of precipitation in Alberta are not large. This is also shown by the fact that the concentration of Na^+ ion is not among the higher values. Therefore, the corrections by equation 1.12 are insignificant compared to the precision of the correlations in Figures 1.4 and 1.5.

2.4 Correlations Among Different Acidity Results

The correlations between precipitation acidity measured by three different methods (pH, titration with purging, and cation - anion balance) are summarized below (assuming that the acidic contribution is not pH dependent):

$$(10^{-pH} - 10^{-\text{endpoint pH}}) - [HCO_3^-] = (\text{Acidity})_{\text{titration}} \qquad (1.13)$$

$$10^{-pH} - [HCO_3^-] = (\text{Acidity})_{\text{cation-anion balance}} \qquad (1.14)$$

$$(\text{Acidity})_{\text{titration}} + 10^{-\text{endpoint pH}} = (\text{Acidity})_{\text{cation-anion balance}} \qquad (1.15)$$

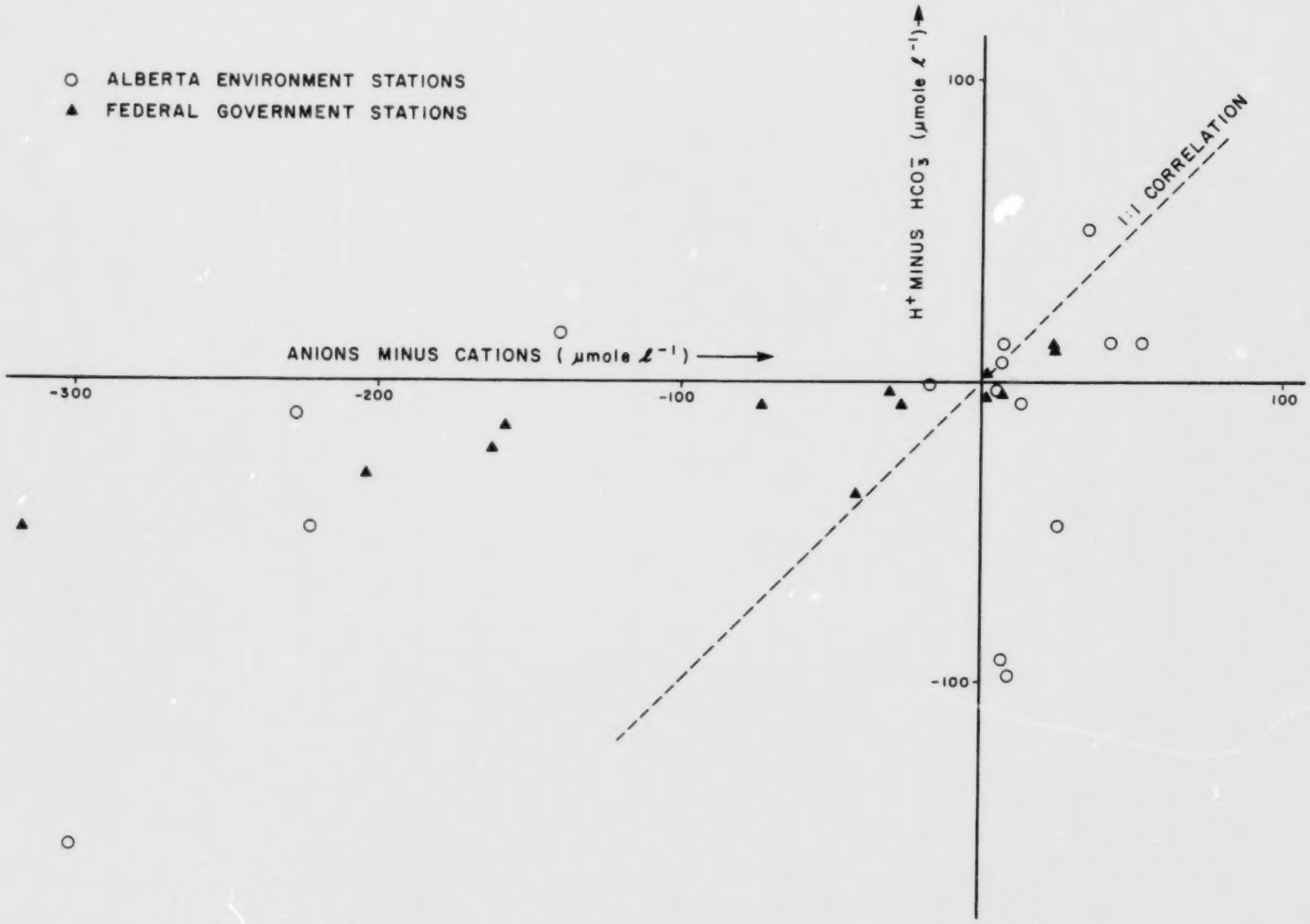

FIGURE 1.5 CORRELATION BETWEEN "H^+ MINUS HCO_3^-" AND "ANIONS MINUS CATIONS" AFTER REMOVING CONTRIBUTION FROM SEA SALTS

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where all concentrations are in units of mole litre^{-1}. The exact quantitative correlation between Gran's plot results and others is not possible unless the endpoint pH is known. However, it is generally accepted that the strong acidity and pH measurement results are directly comparable, whereas the total acidity is normally higher than the acidity by pH measurement. Thus, by using the relationship of $(\text{strong acidity})_{\text{Gran}} \approx (\text{acidity})_{\text{pH}}$, intercomparison can also be made between Gran's plot results and cation - anion balance. The exclusion or inclusion of the HCO_3^- concentration in equation 1.14 is then dependent on whether or not purging is done prior to titration.

3. Methods for Averaging Acidity

Different methods have been used to determine mean acidity from two or more samples. It is unfortunate that different methods can lead to quite different results especially if the range is large. A description and discussion of the commonly used methods follows.

3.1 pH Average

The pH average is an average of acidity in logarithmic scale. It is commonly used as a measure of average acidity on precipitation collected in a particular station or in a region where no large variation in acidity is expected. It has the advantage of being simple to calculate, but as the

term implies, it literally only gives the mean of different pH values. Two types of pH averages may be determined.

(1) Normal pH Average

$$\text{pH (average)} = \frac{\text{pH (1)} + \text{pH (2)} + \ldots \text{pH (n)}}{n}$$

(2) Weighted pH Average

$$\text{pH (average)} = \frac{\text{vol(1)xpH(1)+vol(2)xpH(2)} + \ldots \text{vol(n)xpH(n)}}{\text{vol(1)} + \text{vol(2)} + \ldots \text{vol(n)}}$$

Very often, a pH average is used to represent the mean of repeated measurements on samples from the same lot. For that purpose, the normal pH average should be used. The weighted pH average is used to take into account of the amount of precipitation each sample represents. As acidity is a measure of protons and pH is related to a logarithmic scale of proton concentration, it would be expected that an average on the logarithmic scale (pH average) will weigh heavier on lower values compared with that on the corresponding linear scale (H^+ concentration average). The difference would be insignificant if the range is small. In order to compare with the other averaging methods, two samples of equal volume, (a) at pH 7.0 and (b) at pH 5.0 are considered. The weighted pH average (as well as the normal pH average in this particular case) would be pH = 6.0.

3.2 Weighted H^+ Concentration Average

The average is obtained by first calculating the H^+ concentration for each sample and multiplying by the corresponding volume which the sample

represents. These are then summed, divided by the total volume and the resultant H^+ concentration may be reconverted to the pH scale.

Referring back to the two samples of equal volume:

sample (a)	pH = 7	sample (b) pH = 5
	$[H^+] = 10^{-7}$ mole l^{-1}	$[H^+] = 10^{-5}$ mole l^{-1}
	volume = V	volume = V

$$\text{Average } [H^+] = \frac{10^{-7} \times V + 10^{-5} \times V}{2V}$$

$$= 5.05 \times 10^{-6} \text{ mole } l^{-1}$$

$$pH = -\log [H^+] = 5.30$$

The above calculation confirms that a linear average does give a higher value than a logarithmic average (higher acidity, lower pH). The linear average is preferred because it is more sensitive to minor fluctuations, and it gives a true average of H^+ concentration which is directly related to the definition of acidity.

It should be noted that the calculated weighted average H^+ concentration would <u>not</u> be the same as the measured value if the samples (a) and (b) are physically mixed together. This is because of the complication from the presence of the CO_2 - H_2O equilibrium 1.2. If $[CO_2]$ is taken to be the atmospheric CO_2 partial pressure,

$$CO_2 + H_2O = H^+ + HCO_3^- \qquad (1.2)$$

$$\frac{[H^+]\,[HCO_3^-]}{[CO_2]_g} = 10^{-7.81} \text{ at } 25°C \qquad (1.3)$$

at STP (standard temperature and pressure), $[H^+][HCO_3^-] = 10^{-11.31}$ when the precipitation is in equilibrium with the atmospheric CO_2. For sample (a) at pH = 7, $[HCO_3^-] = 4.90 \times 10^{-5}$ mole l^{-1}; and for sample (b) at pH = 5, $[HCO_3^-] = 4.90 \times 10^{-7}$ mole l^{-1}. Therefore, the weighted average of $[HCO_3^-]$ is 2.47×10^{-5} mole l^{-1}. For a solution at pH 5.30 (from the weighted H^+ average) with $[HCO_3^-] = 2.47 \times 10^{-5}$ mole l^{-1} in equilibrium with CO_2 in the atmosphere, the partial pressure of CO_2 has to be about 8000 ppm (in contrast to 316 ppm in standard atmosphere). If samples (a) and (b) are physically mixed together, equilibrium 1.2 will adjust itself by reacting equal amounts of H^+ and HCO_3^- to form CO_2 and H_2O until the conditions set up in equation 1.3 (or equation 1.4 when under normal atmosphere) are satisfied. The resulting pH and HCO_3^- after mixing can be calculated in the following manner:

Let X = concentrations of H^+ or HCO_3^- reacted

$$[H^+]\,[HCO_3^-] = 10^{-11.31}$$

$$(5.05 \times 10^{-6} - X)\,(2.47 \times 10^{-5} - X) = 10^{-11.31}$$

$$X = 4.8 \times 10^{-6} \text{ mole } l^{-1}$$

After mixing samples (a) and (b),

resulting $[H^+] = 2.5 \times 10^{-7}$ mole l^{-1}

pH = 6.6

$[HCO_3^-] = 1.99 \times 10^{-5}$ mole l^{-1}

The calculated results show that with equal volume of sample (a) at pH 7 and sample (b) at pH 5, the weighted H^+ average gives a pH of 5.3. But when samples (a) and (b) are mixed together, the resulting pH would be 6.6. The implication of the results is important. It shows that if two event precipitation samples are collected and analyzed, the calculated average acidity would not be the same as the acidity measured if the two samples are allowed to accumulate in the collection device prior to analysis. The same effect would appear if a single event is divided into several sampling periods. Expressing precipitation acidity is not so problematical as long as the sampling period is well defined, because it is normally accepted that methods of averaging do not account for possible chemical reactions. There is greater difficulty when the H^+ loading on soil is considered.

3.3 Weighted "Effective" H^+ Concentration Average

The weighted $[H^+]$ average obtained by taking CO_2 - H_2O equilibrium into consideration (allowing physical mixing) may be obtained in another way, that is, from averaging "$[H^+]$ minus $[HCO_3^-]$" or "effective $[H^+]$"

values. The "$[H^+]$ minus $[HCO_3]$" or "effective $[H^+]$" has positive values for acidic precipitation (pH<5.6), zero for neutral precipitation (pH 5.6) and negative values for basic precipitation (pH>5.6). The value of "$[H^+]$ minus $[HCO_3^-]$" always assumes that HCO_3^- concentration is governed by the CO_2 - H_2O equilibrium. That is why the average $[H^+]$ obtained by averaging "$[H^+]$ minus $[HCO_3^-]$" is equivalent to that by allowing adjustment of CO_2 - H_2O equilibrium (physical mixing). This can be illustrated by using the same example as before:

(all concentrations in mole l^{-1})

sample (a): pH = 7

$[H^+] = 10^{-7}$

$[HCO_3^-] = 4.90 \times 10^{-5}$

sample (b): pH = 5

$[H^+] = 10^{-5}$

$[HCO_3^-] = 4.90 \times 10^{-7}$

*assuming precipitation in equilibrium with 316 ppm CO_2.

$[H^+] - [HCO_3^-] = -4.89 \times 10^{-5}$

$[H^+] - [HCO_3^-] = 9.51 \times 10^{-6}$

weighted average "$[H^+] - [HCO_3^-]$" = -1.97×10^{-5}

In order to convert back to the pH scale, the total H^+ concentration has to be obtained. This may be achieved by solving the following equations simultaneously

$$[H^+] - [HCO_3^-] = -1.97 \times 10^{-5} \quad \ldots\ldots(1)$$

$$[H^+]\,[HCO_3^-] = 10^{-11.31} \quad \ldots\ldots\ldots(2)$$

On substitution, the following quadratic equation results:

$$[H^+]^2 + 1.97 \times 10^{-5} [H^+] - 4.90 \times 10^{-12} = 0$$

It yields $[H^+] = 2.46 \times 10^{-7}$ mole l^{-1} and a pH value of 6.6. The resulting equilibrium $[HCO_3^-]$ is 1.99×10^{-5} mole l^{-1}. The results are identical to those from the method of weighted $[H^+]$ average for physical mixing (allowing adjustment of chemical equilibrium).

The above comparison indicates that for a dynamic system, the concentration term of "hydrogen ions minus bicarbonate ions" is a more appropriate measure of acidity. This is the case when precipitation falls onto the soil which acts as an acid or base sink. The hydrogen ion loading on soil is a continuous process. The system will adjust itself continuously; trying to be in harmony with the environment according to various equilibria requirements. It is unfortunate that "$[H^+]$ minus $[HCO_3^-]$" is not more widely used as a measure of precipitation acidity. As it turns out, two of the three methods of acidity measurement discussed in the present report can measure this quantity instead of the actual H^+ concentration. Of course, interconversion between $[H^+]$ and "$[H^+] - [HCO_3^-]$" is possible provided that the equilibrium partial pressure of CO_2 in the atmosphere is known.

As a comparison, the average acidity for the two samples of equal volume (sample (a): pH 7 and sample (b): pH 5) calculated by different methods described above are summarized below:

	Averaging Method	Average $[H^+]$ (mole L^{-1})	Resulting pH
1.	"Normal" pH average	10^{-6}	6.0
2.	Weighted pH average	10^{-6}	6.0
3.	Weighted $[H^+]$ average	5.05×10^{-6}	5.3
4.	Weighted $[H^+]$ average (allowing physical mixing)	2.5×10^{-7}	6.6
5.	Weighted "effective" $[H^+]$ average	2.5×10^{-7}	6.6

"Normal" pH average should be used only on repeated determination of acidity measurement of a sample. Weighted pH average is not a recommended method. The weighted $[H^+]$ average is the choice in calculating mean acidity in precipitation samples. The weighted $[H^+]$ average (allowing physical mixing) demonstrates the fact that interpretation of average acidity in precipitation is not a straightforward matter. Its use is not widespread because of traditional thinking that is concerned only with the concentration of protons. No interaction among samples is presumed. This is true for sampling on an event basis but not for sampling on a bulk (time) basis. The weighted "effective" $[H^+]$ average is another way of getting weighted $[H^+]$ average with allowance for physical mixing. They both give identical results, and may provide a better representation of the acidity loading in soil.

When results of precipitation acidity are presented the measurement methods must be described in detail because there is presently no universally acceptable method for measuring and reporting precipitation acidity. Care has to be exercised in interpreting the data especially when comparisons of data are to be made.

3.4 Experimental Results on Averaging Acidity

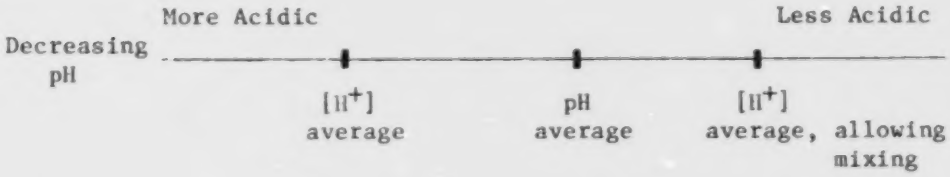
An experiment on averaging acidity of two precipitation samples was carried out by Henry Bertram at the Alberta Environmental Centre. The pH of each of the two samples, #213 and #220, and of a 50/50 mixture were monitored over a 24-hour period. The results obtained are reproduced as follows:

Time (hr:min)	pH			Remarks
	#213	#220	50/50 Mixture	
11:00	4.95	6.55	6.60	Start monitoring, samples still cold, not yet at equilibrium
13:00	4.85	6.75	6.48	
16:30	4.95	6.75	6.40	
9:00	4.90	6.80	6.45	Next day
pH at equilibrium	4.90	6.77	6.44	Average Values

The average acidity for the two samples of equal volume (sample (a): pH 4.90; sample (b): pH 6.77) may be calculated by different methods as described in this section. A comparison of the calculated values and the experimental values are shown below:

*Experimental value	pH 6.44
*Calculated, pH average	pH 5.84
*Calculated, Weighted $[H^+]$ average	pH 5.20
*Calculated, Weighted $[H^+]$ average, but allowing physical mixing (or, weighted "effective" $[H^+]$ average)	pH 6.25

The model using weighted $[H^+]$, but allowing chemical equilibrium to take place (Section 3.2), or the weighted "effective" $[H^+]$ (Section 3.3) yields an average value which is very close to the experimental value. Calculated pH = 6.25, and measured pH = 6.44 correspond to an error percentage of 3%. Both "normal" pH average and weighted $[H^+]$ average yield lower pH (more acidic) values. This in in agreement with the discussion associated with the derivation of individual models.



4. Temperature Effects on Acidity Measurement

The possible effects of temperature on acidity should be investigated especially for places where the ambient (sampling) temperature has large diurnal or seasonal variations. The ability of a gaseous acidifying agent to acidify precipitation depends on its solubility and the corresponding ionization constant. (Only the first ionization constant is important if the higher order ionization constant(s) is much smaller in magnitude). The temperature effects on the two parameters can be scrutinized more closely by looking at two specific examples: carbon dioxide and sulphur dioxide.

4.1 Temperature Dependence of the Acidifying Ability of Carbon Dioxide

The transformation sequence which is of interest is $[CO_2]_{air} \longrightarrow [CO_2]_{rain} \longrightarrow [H^+]_{rain}$. The corresponding chemical reactions can be written as follows:

$$[CO_2]_{air} = [CO_2]_{rain(r)} \qquad (1.16)$$

$$[CO_2]_r + H_2O_{(aq)} = [H^+]_r + [HCO_3^-]_r \qquad (1.17)$$

From reaction (1.16),

$$k_H = [CO_2]_{rain}/[CO_2]_{air} \qquad \text{Henry's constant}$$

and from reaction (1.17),

$$K = \frac{[H^+]_r\,[HCO_3^-]_r}{[CO_2]_{rain}} \qquad \text{1st ionization constant}$$

The overall equilibrium concentrations are governed by the product of the two constants.

$$k_H K = \frac{[H^+]_r \, [HCO_3^-]_r}{[CO_2]_{rain}} \qquad (1.18)$$

Assuming absence of other ionization reactions, charge neutrality requires that $[H^+] = [HCO_3^-]$.

$$k_H K = \frac{[H^+]_r^2}{[CO_2]_{air}} \qquad (1.19)$$

Therefore, the temperature effects on acidification by the gas depend on the temperature dependence of Henry's constant and ionization constant. For CO_2, the effects were described empirically from 0°C to 50°C by Harned and Davis (1943).

$$-\log k_H = \frac{-2385.73}{T} + 14.0184 - 0.0152642T \qquad (1.20)$$

$$\log K = \frac{-3404.71}{T} + 14.8435 - 0.032786T \qquad (1.21)$$

where T is the absolute temperature, $k_H = m_{CO_2}/P_{CO_2}$ and K is defined as above. All solution terms are in units of molality (# mole per 1000 g of solution), and the gaseous term is in unit of atmospheric pressure. Numerically the temperature effects are illustrated in the following table:

Temperature (°C)	k_H	K	$k_H K$
0	7.676×10^{-2}	2.651×10^{-7}	2.035×10^{-8}
15	4.565×10^{-2}	3.806×10^{-7}	1.737×10^{-8}
25	3.423×10^{-2}	4.456×10^{-7}	1.525×10^{-8}
30	3.011×10^{-2}	4.713×10^{-7}	1.419×10^{-8}

Although the solubility of CO_2 decreases as the temperature increases, its effect is offset by the corresponding increase in the ionization constant. The overall effect is that $[CO_2]_{air} \longrightarrow [H^+]_{rain}$ is not temperature sensitive. This can be shown by calculating the expected pH of "neutral" precipitation (in equilibrium with 316 ppm CO_2) at various temperatures using the above $k_H K$ values.

Temperature (°C)	Expected pH = $-\log (k_H K \times 3.16 \times 10^{-4})^{\frac{1}{2}}$
0	5.56
15	5.63
25	5.66
30	5.67

The temperature insensitivity of the acidic contribution of CO_2 removes one complexity from the precipitation chemistry system.

4.2 Temperature Dependence of the Acidifying Ability of Sulphur Dioxide

A similar transformation sequence of $[SO_2]_{air} \longrightarrow [SO_2]_{rain} \longrightarrow [H^+]_{rain}$ can be written for sulphur dioxide. The formulations adopted by Barrie (1978,1981) are used to illustrate another way of defining chemical terms

$$[SO_2]_{air} = [SO_2 \cdot H_2O]_{rain(r)} \qquad (1.22)$$

$$[SO_2 \cdot H_2O]_r = [H^+]_r + [HSO_3^-]_r \qquad (1.23)$$

$$[HSO_3^-]_r = [H^+]_r + [SO_3^{2-}]_r \qquad (1.24)$$

The choice of using $[SO_2 \cdot H_2O]_{rain}$ instead of $[SO_2]_{rain}$ is arbitrary. The corresponding equilibrium constants are shown below (K for equation 1.24 is ignored):

$$k_H' = [SO_2 \cdot H_2O]_{rain}/[SO_2]_{air} \qquad \text{Henry's constant}$$

$$K' = \frac{[H^+]_r\,[HSO_3^-]_r}{[SO_2 \cdot H_2O]_{rain}} \qquad \text{1st ionization constant}$$

$$k_H'K' = \frac{[H^+]_r\,[HSO_3^-]_r}{[SO_2]_{air}} \qquad (1.25)$$

Although the numerical values of k_H' and K' will be affected by the choice of the model (because of the difference in molecular weight between $SO_2 \cdot H_2O$ and SO_2), the product of $k_H'K'$ is invariant. From the sequence, it is seen that SO_2 in aqueous solution may exist as one of the three possible forms: physically dissolved SO_2 $(SO_2 \cdot H_2O)aq$, bisulphite ion $(HSO_3^-)aq$, or even sulphite ion $(SO_3^{2-})aq$. In the pH range common to precipitation (pH 3-6), Barrie (1978) showed that over 90% of the SO_2 in solution is in the form of bisulphite ion. Since the derivation assumes equlibrium between SO_2 in the air and SO_2 in the precipitation, the relaxation time of the equilibrium 1.22 should be small in comparison with the rate of change in gas phase concentration. Hales (1978) suggested that for SO_2 form a point source, the above equilibrium scavenging condition is usually satisfied beyond 20 stack heights of the point source. Under such conditions, the washout ratio, W_{SO_2}, which represents the ratio of SO_2 scavenged by precipitation to that in air may be approximated by expression 1.26.

$$W_{SO_2} = \frac{[SO_2]_{rain}}{[SO_2]_{air}} \approx \frac{[HSO_3^-]_{rain}}{[SO_2]_{air}} = \frac{k_H'K'}{[H^+]_r} \qquad (1.26)$$

The efficiency of capturing gaseous SO_2 by precipitation thus depends on the pH of the precipitation and the product of the two constants, k_H' and K', which are temperature dependent. The temperature dependence of the acidic contribution of SO_2 has been examined by Barrie (1981). Over the temperature range of 0°C - 30°C, the correlation between $k_H'K'$ and T(°K) follows the empirical equation (Barrie, 1981),

$$k_H'K' = 6.22 \times 10^{-8} \exp (4755.5/T) \qquad (1.27)$$

where all (gaseous and solution) concentration terms are in moles per litre. The numerical variations with temperature showing individual trends are shown below (Barrie, 1981):

Temperature (°C)	k_H	K	k_HK
0	73.5	3.1×10^{-2}	2.3
15	41.5	2.2×10^{-2}	0.91
25	30.3	1.7×10^{-2}	0.53

Unlike the case with CO_2, the solubility as well as the ionization constant decrease with an increase in temperature for SO_2. That is, for a fixed concentration of $[SO_2]_{air}$, the acidity of precipitation would be enhanced at lower temperature, provided that equilibrium is reached. This has an implication that if the field temperature is much lower than the laboratory temperature, the acidity recorded in the field will be higher than that measured in the laboratory (if equilibrium prevails).

One has to be cautious about the acidifying sequence of SO_2 described above. It is observed that equation 1.25 cannot explain the total precipitation acidity attributable to SO_2 in the air. Dissolved SO_2 is eventually oxidized to SO_4^{2-} either in some natural receptors (e.g. ocean, lake and soil) or in the gaseous phase during long-term transport. In the latter

case, if only SO_2 is considered, it has been suggested by Friend (1978) that the heterogeneous oxidation of either or both HSO_3^- and SO_3^- to SO_4^{2-} can build up acidity to a limiting pH of ~3 (Le Chatelier's principle prevents further absorption of SO_2 beyond pH 3 based on equilibrium considerations). The oxidation step is known to be quite fast in the presence of catalytic ions, namely Mn^{2+} and Fe^{3+}.

$$[SO_2]_{air} \rightleftharpoons [SO_2 \cdot H_2O]_{rain} \rightleftharpoons \underset{[HSO_3^-]}{[H^+]} \rightleftharpoons \underset{[SO_3^{2-}]}{2[H^+]} \xrightarrow[\text{Catalyst}]{O_2} [SO_4^{2-}] + 2[H^+] \qquad (1.28)$$

Hence, two hydrogen ions are released for each SO_2 molecule deposited in rain instead of one as indicated in equations 1.23 and 1.25. The eventual oxidation of HSO_3^- and/or SO_3^{2-} to SO_4^{2-} enables the formation of a relatively strong acid solution because of the large first and second ionization constants for sulphuric acid. The extent of $[H^+]$ contribution ($1H^+$ to $2H^+$) per dissolved SO_2 molecule thus depends on how complete the oxidation is prior to the analysis of precipitation samples. In order to have a complete picture on acidification of precipitation by SO_2, HSO_3^- ion (major form of dissolved SO_2) should be analyzed separately. The HSO_3^- ion can also be determined from the difference of SO_4^{2-} ion concentration before and after the precipitation sample is subjected to a complete oxidation process. The existence of a correlation between $[H^+]$ and $[SO_4^{2-}]$, even if present, does not necessarily mean that HSO_3^- ion is not important, but may only imply that they are correlated by chemical "pseudo-

equilibria". The same could be said to other components of acidic rain such as nitrogen oxides. Until cycles of other acidifying agents are quantitatively better understood, the sulphur cycle would be favored as a model for predicting precipitation acidity.

PRECIPITATION CHEMISTRY

II. SPECIFIC CONDUCTANCE & ION CONCENTRATIONS

II. SPECIFIC CONDUCTANCE AND ION CONCENTRATIONS

1. Introduction

The conductance of a precipitation sample is a measure of how well it will conduct electricity. It is related to the concentration and the type of ions in it. Inorganic acids, bases and salts are generally good conductors because they ionize to a large extent in aqueous media, whereas organic compounds generally are not. Therefore, conductance can be used as a measure of total inorganic ion content.

The objective of this study is to derive a correlation betwen specific conductance measurement and the measurement of individual ion concentrations in precipitation samples. If a correlation does exist between them, it can be used as a means of quality assurance on the analysis of precipitation samples.

2. Glossary

Several terms used in conductance measurement have to be defined. The conductance, L, of an electrolyte solution is defined as the inverse of its resistance, R. Since conductance is dependent on the length and area under measure, some more explicit terms are used for better comparison among different electrolytes. Specific conductance, K, is the conductance of a 1-cm cube of the solution of electrolyte. To enable comparison of electrolytes on an electrically equivalent basis (same number of total positive

and negative charges), the term equivalent conductance, Λ, is generated. Equivalent conductance may be considered as the conductance of the electrolyte solution 1 cm in length, with a cross-section large enough to contain one equivalent of the electrolyte (#equivalent = weight/[molecular weight x #charge]); one equivalent of any electrolyte, upon complete dissociation, produces the same effective number of charge carrying species). Mathematically, the terms conductance L, specific conductance K, and equivalent conductance Λ can be expressed as in the following equations (Barrow 1966):

$$L = \frac{1}{R} \qquad (2.1)$$

$$K = L\frac{\ell}{A} \qquad (2.2)$$

$$\Lambda = \frac{1000}{c} K \qquad (2.3)$$

where R is resistance in ohm; ℓ is length (cm) and A is the area (cm^2) of solution under measure; c is the concentration of electrolyte in number of equivalent per 1 litre (1000 cm^3). The resulting unit for L is ohm^{-1} (or mho, or siemen), for K is $ohm^{-1}cm^{-1}$, and for Λ is $ohm^{-1}cm^2$ equivalent $^{-1}$.

3. Theoretical Correlation

The law of independent migration of ions (by F.W. Kohlrausch, 1876) which is true for infinite dilution suggests that at infinite dilution, the conductance of an electrolyte, for example, NaCl, depends on independent contributions from Na^+ and Cl^-. In this way, equivalent ionic conductance at infinite dilution, λ_o^+ or λ_o^-, is introduced and the following relationship can be written for the limit of infinite dilution:

$$\lim_{c \to o} \Lambda = \Lambda_o = \lambda_o^+ + \lambda_o^- \qquad (2.4)$$

for example, $\Lambda_o(NaCl) = \lambda_o(Na^+) + \lambda_o(Cl^-)$

where Λ_o is the equivalent conductance at infinite dilution. Because λ_o is an intensive property which is characteristic of an individual ion, the independent contribution of the ions at infinite dilution can be used for deducing the upper limit of the equivalent conductance for the corresponding electrolyte. (Equivalent conductance decreases non-linearly with increasing concentration from infinite dilution. The decrease is much more rapid for weak electrolytes than for strong electrolytes.)

Precipitation normally has a total ionic concentration of about $\sim 10^{-4}$ equivalent per litre (#equivalent = weight/(molecular weight x # charge)). The law of independent migration of ions should thus hold. The expected conductance could be calculated from the concentration of all ions which make contributions to the total conductance. Since specific conductance (conductance of a 1-cm cube of solution) is an easily measureable experimental quantity, a comparison of experimental specific conductance and calculated specific conductance is chosen for the correlation study. On substituting equation 2.4 into 2.3, equation 2.5 which is good only for infinite dilution may be obtained.

$$K = \frac{1}{1000} (\lambda_o^+ + \lambda_o^-)c \quad \text{for} \quad c \to o \qquad (2.5)$$

It is by expanding equation 2.5 to cover multi-ions at infinite dilution that specific conductance of precipitation samples may be calculated. The resulting expression is shown as equation 2.6,

$$K = \frac{1}{1000} \Sigma(\lambda_o c)_i \qquad (2.6)$$

where specific conductance K is in siemen cm^{-1} (or $ohm^{-1}cm^{-1}$), ionic equivalent conductance λ_o is in siemen cm^2 $equivalent^{-1}$, and concentration c is in equivalent per litre. The factor 1000 is for balancing of units in the expression.

The cations commonly found in precipitation samples are NH_4^+, Na^+, K^+, Ca^{2+}, Mg^{2+} and H^+. The major anions are SO_4^{2-}, NO_3^-, Cl^- and HCO_3^-. The equivalent conductance of the separate ions at infinite dilution and 25°C are tabulated in Table 2.1. Based on Table 2.1 and equation 2.6, a working expression for calculating specific conductance of a precipitation sample may be written as follows:

$$\begin{aligned} K_{calc} = {} & 10^{-3} \times [74.5(NH_4^+) + 50.9(Na^+) + 74.5(K^+) \\ & + 60.0(Ca^{2+}) + 53.1(Mg^{2+}) + 350(H^+) \\ & + 79.0(SO_4^{2-}) + 70.6(NO_3^-) + 75.5(Cl^-) \\ & + 43.5(HCO_3^-)] \end{aligned} \qquad (2.7)$$

TABLE 2.1

EQUIVALENT CONDUCTANCE OF THE SEPARATE IONS AT INFINITE DILUTION AND 25°C[1]

Cations	Equivalent Conductance $\lambda_o(ohm^{-1}cm^2eq^{-1})$*	Anions	Equivalent Conductance $\lambda_o(ohm^{-1}cm^2eq^{-1})$*
NH_4^+	74.5	SO_4^{2-}	79.0
Na^+	50.9	NO_3^-	70.6
K^+	74.5	Cl^-	75.5
Ca^{2+}	60.0	HCO_3^-	43.5
Mg^{2+}	53.1		
H^+	350	OH^-	192

[1] From "Handbook of Chemistry and Physics. 52nd Edition," p.D123, except for Mg^{2+} which is from "Textbook of Physical Chemistry," by S. Glasstone, 2nd Edition, 1946, p.894.

*eq = equivalent = weight/(molecular weight x #charge in ion)

K_{calc} would be in siemen cm^{-1} if the ionic concentrations are in #equivalent/litre. More commonly for precipitation analysis, ion concentrations would be in # μequivalent/litre and K_{meas} is then in μsiemen cm^{-1} (or $\mu ohm^{-1}cm^{-1}$). It should be noted from table 2.1 that the range of ionic equivalent conductance for most ions is between 40-80 $ohm^{-1}cm^2eq^{-1}$. The only exceptions are H^+ and OH^- which have values of 350 and 192 $ohm^{-1}cm^2eq^{-1}$ respectively. The higher values for H^+ and OH^- are due to their high ionic mobility in aqueous media via H-bonding. The disparate conductivity of H^+/OH^- compared to that of other ions calls for attention when the correlation between specific conductance and ion concentration is applied to precipitation samples with pH outside the range of 4-9. Below pH 4, the conductivity due to hydrogen ions outweighs that from other ions. Above pH 9, the contribution from hydroxyl ion, which is not included in equation 2.7, would be significant toward total conductivity. The contribution by hydroxyl ion can be included by adding the term "192 x $[OH^-]$" to the series of individual ionic specific conductance in equation 2.7. Even so, in both cases (pH<4 and pH>9), the correlation is weighed so heavily on H^+ or OH^- that any error, if present on other ion concentrations, would not significantly alter the correlation.

A rough conductivity check analysis as described in American Public Health Association's Standard Methods (1980) should also be mentioned here. In most natural water, the following approximate relation can be formulated (based on the same principle):

specific conductance ($\mu ohm^{-1}cm^{-1}$ at 25°C)

x constant (0.55 - 0.70)

= total filtrable residue (mg/l) (2.8)

The approximate check will reveal gross mistakes in analysis. Water with high salinity (or high ion concentration) would have the constant much higher than 0.7 because infinite dilution no longer applies, whereas for highly acidic or alkaline water, the constant will be much less than 0.55 because of the relatively large ionic conductivity of H^+ and OH^-.

4. Testing of the Theoretical Correlation

Twenty-eight data sets were chosen from the Alberta Environment Precipitation Quality Data Summary from April 1978 to December 1979. Fifteen data sets were from Alberta Environment stations, and the remaining were from Federal Government stations. Completeness in cation - anion analyses is the criterion used in selecting the data sets. They are the same data sets as those chosen in comparing acidity measurements in Part I. The ions analyzed were NH_4^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, SO_4^{2-}, NO_3^- and Cl^-. In order to use expression 2.7, concentrations of H^+ and HCO_3^- are also required. $[H^+]$ was calculated from the results of pH measurement, $[H^+] = 10^{-pH}$. By assuming equilibrium between atmospheric CO_2 (316 ppm) and precipitation samples at 25°C, $[HCO_3^-] = 10^{-11.31}/[H^+]$. The calculated specific conductance K_{calc} (by equation 2.7) for the twenty-eight data sets are summarized in table 2.2, together with the corresponding measured specific conductance (K_{meas}) values. The ratio of K_{meas}/K_{calc} which is a data quality index is listed in table 2.2. Also presented in the table is another data quality index, [cations]/[anions] ratio, for all data sets. It is expected that a 1:1 correlation between K_{meas} and K_{calc} would result if the assumption of infinite dilution holds. As the ionic concentration

TABLE 2.2

DATA ON MEASURED AND CALCULATED SPECIFIC CONDUCTANCE RATIO AND CATION - ANION CONCENTRATION RATIO

I. Alberta Environment Stations

Sample #	Measured Specific Conductance, K_{meas} in μsiemen cm^{-1}	Calculated Specific Conductance, K_{calc} in μsiemen cm^{-1}	$\frac{K_{meas}}{K_{calc}}$ Ratio	$\frac{[Cations]}{[Anions]}$ Ratio
1	32.3	18.5	1.7	0.4
2	18.4	14.1	1.3	0.4
3	85.4	72.4	1.2	1.5
4	15.5	12.8	1.2	0.9
5	21.2	15.9	1.3	0.9
6	13.3	9.5	1.4	1.3
7	18.5	17.9	1.0	1.2
8	7.0	9.9	0.7	1.2
9	16.6	19.8	0.8	0.5
10	47.0	42.2	1.1	1.7
11	14.7	36.6	0.4	1.0
12	23.4	29.1	0.8	1.2
13	54.3	43.7	1.2	1.5
14	15.5	20.0	0.8	0.8
15	7.6	10.4	0.7	0.5

TABLE 2.2 (continued)

II. Federal Government Stations

Sample #	Measured Specific Conductance, K_{meas} in μsiemen cm^{-1}	Calculated Specific Conductance, K_{calc} in μsiemen cm^{-1}	$\frac{K_{meas}}{K_{calc}}$ Ratio	$\frac{[Cations]}{[Anions]}$ Ratio
16	39.9	40.3	1.0	1.6
17	19.1	21.1	0.9	1.7
18	17.1	20.7	0.8	1.1
19	10.2	11.1	0.9	1.0
20	10.0	9.8	1.0	1.0
21	36.6	34.1	1.1	1.7
22	57.7	43.1	1.3	2.2
23	7.6	10.1	0.8	1.4
24	24.0	20.2	1.2	1.0
25	9.0	8.5	1.1	0.8
26	6.8	7.3	0.9	1.2
27	9.8	9.1	1.1	0.7
28	31.8	32.5	1.0	2.4

of a solution increases beyond the tolerable limit of the assumption, it is expected that $K_{meas}/K_{calc} < 1$ with K_{calc} as the upper limit of K_{meas}.

The resulting correlations between K_{meas} and K_{calc} are shown graphically in Figure 2.1. A good one-to-one correlation was observed on the whole. No significant difference was observed between data sets obtained from Alberta Environment stations and those from Federal Government stations. It is interesting to note that the four highest K_{meas} values are larger than the corresponding K_{calc} values, an observation not attributable to concentration effects which should lead to the reverse. All four data sets correspond to high Ca^{2+} concentrations ($\sim 4 \times 10^{-4}$ equivalent/litre) which are an order of magnitude higher than the normal Ca^{2+} concentration in precipitation. They were all from southern Alberta stations collected in summer months, namely, Calgary (May 1978, June 1979, July 1979) and Lethbridge (May 1978). It is not clear whether or not the high concentration of calcium ion in precipitation would interfere with the measurement of some parameters in the analysis. As regard to the data presented in Figure 2.1, the following statistics were obtained by least square linear regression analysis of the twenty-eight data sets.

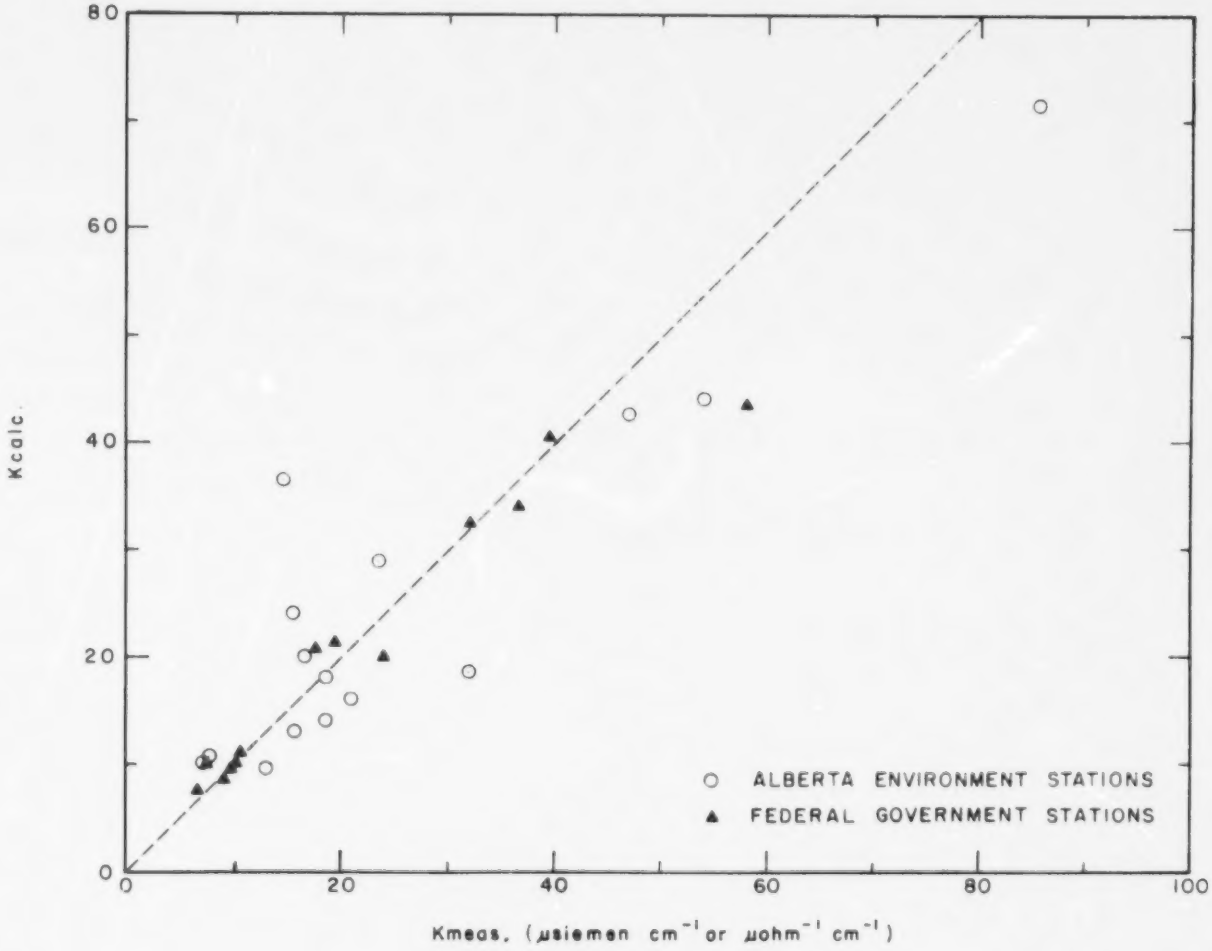


FIGURE 2.1 CORRELATION BETWEEN MEASURED AND CALCULATED SPECIFIC CONDUCTANCE

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Pollution Control Division

	Correlation Coefficient	Slope	Y-intercept
Alberta Environment (15 samples)	0.906	0.744	5.78
Federal Government (13 samples)	0.970	0.794	3.57
TOTAL (28 samples)	0.928	0.764	4.78

The ratio K_{meas}/K_{calc} is used as a data quality index. A value of 1 for the ratio indicates that all parameters from ion analysis and pH measurement do agree with results from specific conductance measurement, an indication of good quality data. Values higher or lower than 1 suggest the deterioration of data quality corresponding to the magnitude of deviation from unity. The frequency distribution of values of K_{meas}/K_{calc} ratio is tabulated as follows

K_{meas}/K_{calc}	$\geq$1.4	1.3	1.2	1.1	1.0	0.9	0.8	0.7	$\leq$0.6
Alberta Environment	2	2	3	1	1		3	2	1
Federal Government		1	1	3	3	3	2		
TOTAL	2	3	4		4	3	5	2	1

mean = 1.03; standard deviation = 0.27

Although the sample size is too small for analysis in terms of distribution statistics, the fact that 86% of the data sets falls within the range of 1.3 - 0.7 suggest satisfactory experimental results.

Another data quality index has been suggested by Peters, Sandhu and Hume (1981). It is the ratio of equivalent concentrations of positive ions to negative ions. Cations considered were NH_4^+, Na^+, K^+, Ca^{2+}, Mg^{2+} and H^+. Anions included were SO_4^{2-}, NO_3^-, Cl^- and HCO_3^-. The ionic ratio for the twenty-eight data sets are shown in Table 2.2. The frequency distribution of the [cations]/[anions] ratio is tabulated as follows:

(CAT)/(AN)	≥1.4	1.3	1.2	1.1	1.0	0.9	0.8	0.7	≤0.6
Alberta Environment	3	1	3		1	2	1		4
Federal Government	6		1	1	3		1	1	4
TOTAL	9	1	4	1	4	2	2	1	4

mean = 1.17; standard deviation = 0.50

A ratio of 1 indicates data of good quality. Any deviation from unity is a measure of deviation from good quality data. It is seen that the variability of this quality index is larger than that of K_{meas}/K_{calc} ratio. The differences are mainly due to different treatments on the results of precipitation analysis. This point is demonstrated in the correlation diagram between K_{meas}/K_{calc} and [cations]/[anions] as shown in Figure 2.2. The lack of correlation suggests that the experimental errors are "transduced" differently in the two approaches. Also, the number of experimental parameters considered are not exactly the same. The present results seem to show that the ratio of measured and calculated specific conductance, K_{meas}/K_{calc}, is a more meaningful quality index for data on chemical analyses of precipitation. It has an advantage of being not very sensitive to the HCO_3^- concentration which is not a direcly measured quantity, but only a calculated value based on equilibrium assumptions.

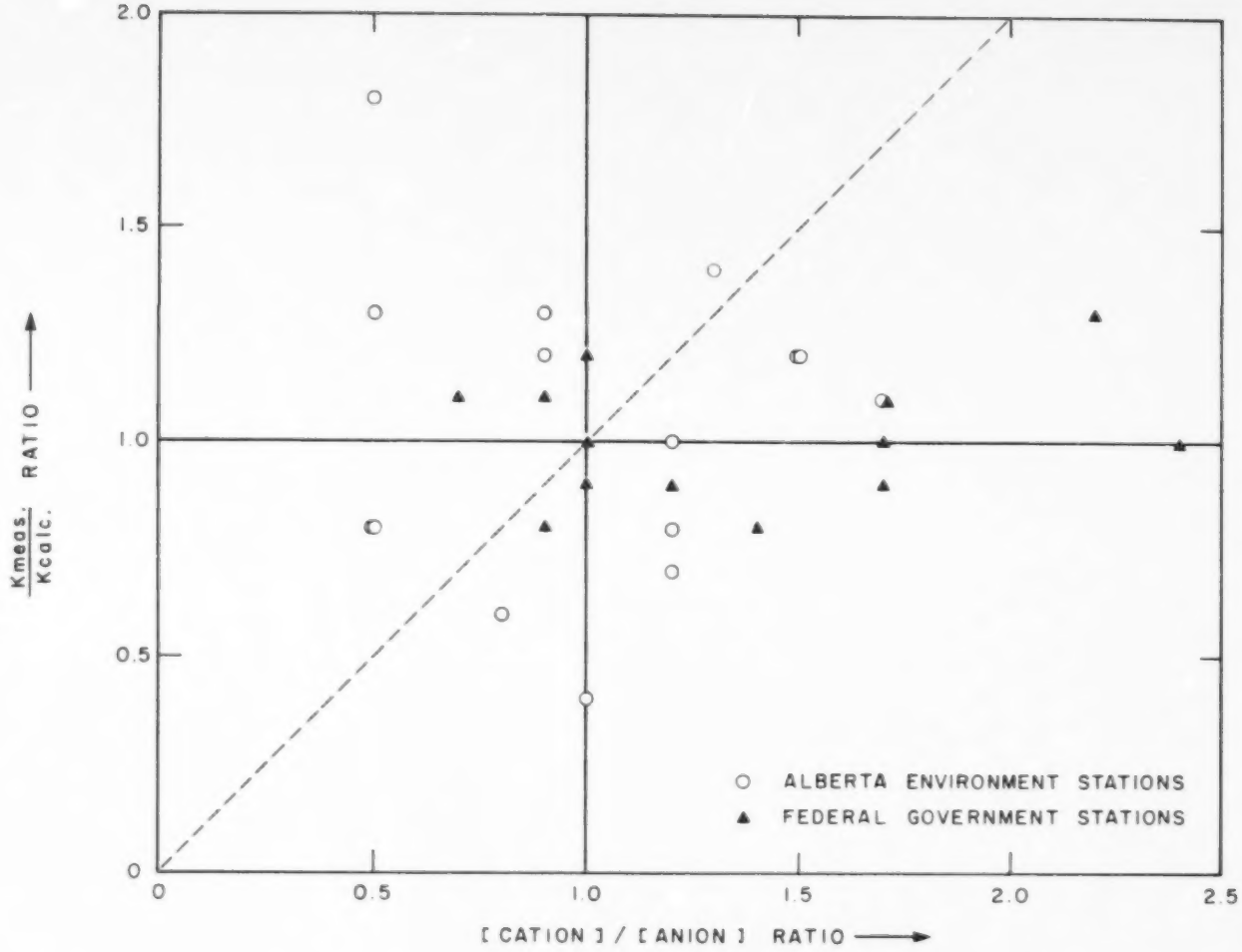

FIGURE 2.2 LACK OF CORRELATION BETWEEN SPECIFIC CONDUCTANCE RATIO AND ION RATIO

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5. Correlations Between Hydrogen Ions and Sulphate Ions or Nitrate Ions in Precipitation

No correlation was observed between $[H^+]$ and $[SO_4^{2-}]$ or $[H^+]$ and $[NO_3^-]$ in the twenty-eight samples studied. The independence of individual concentrations is demonstrated in Figures 2.3 and 2.4. A similar study by Barrie (1981) on precipitation samples collected in Eastern Canada and Eastern U.S.A. showed significant correlations between H^+ and SO_4^{2-} concentrations in many sites. It was concluded that the two parameters are strongly related if the local soil is non-calcareous and the precipitation is acidic, especially if the sampling site is downwind of a major emission source. Poor correlations would be expected if precipitation has pH>5 or the location is limestone-based. The alkaline calcium particles can often get into the precipitation sample in dust form, thus lowering its acidity. Based on the above conclusions, it is not surprising that no correlation was observed in the present data sets. About 80% of the samples examined have pH>5 and most of the land in Alberta has alkaline soil. It should also be noted that no change in precipitation acidity would occur if the input of SO_4^{2-} or NO_3^- is accompanied by similar amounts of basic cations: Na^+, K^+, Ca^{2+}, or Mg^{2+}. That is, the molar equivalent proportionality between SO_4^{2-} or NO_3^- and H^+ would hold only if SO_4^{2-} and NO_3^- are formed from SO_2 and NO_x respectively. It is difficult to pinpoint whether the lack of correlations is due to masking by high calcareous particles in the atmosphere or to the insignificant contribution of SO_4^{2-} or NO_3^- from emission sources.

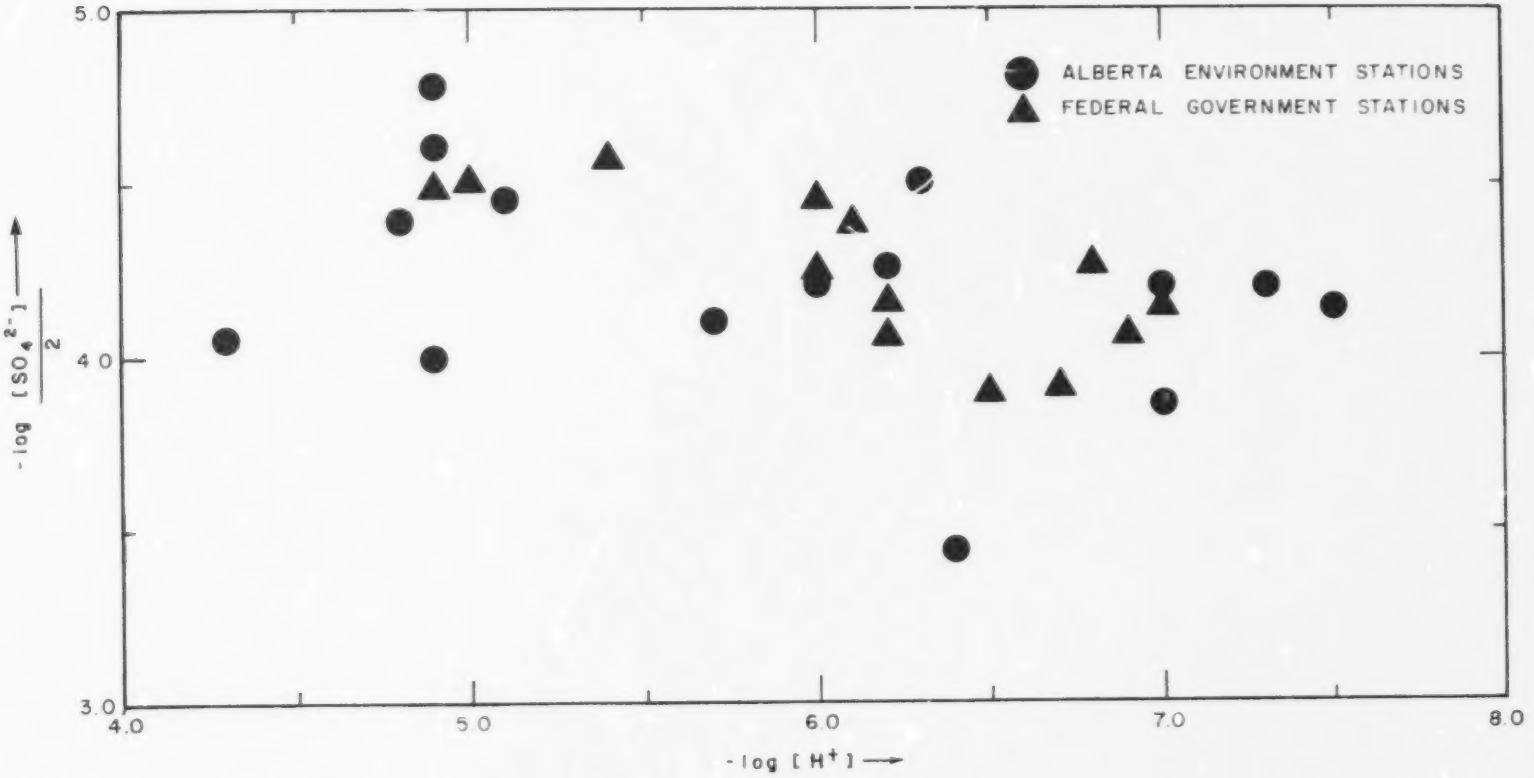

FIGURE 2.3 CORRELATION BETWEEN $[H^+]$ AND $[SO_4^{2-}]$
(CONCENTRATION IN MOLE PER LITRE)

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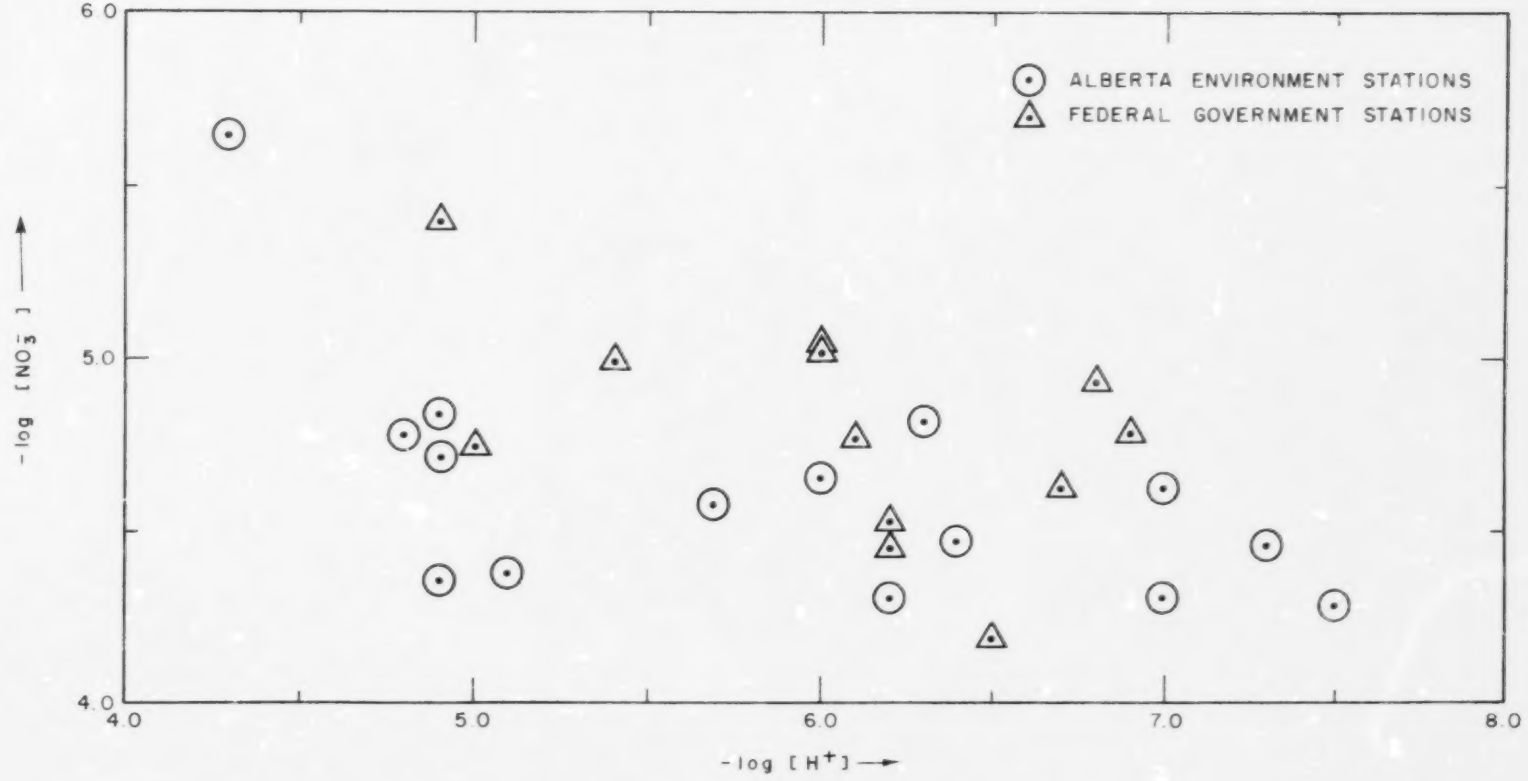

FIGURE 2.4 CORRELATION BETWEEN $[H^+]$ AND $[NO_3^-]$
(CONCENTRATION IN MOLE PER LITRE)

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CONCLUSIONS AND RECOMMENDATIONS

I. PRECIPITATION ACIDITY MEASUREMENTS

1. Precipitation acidity should be determined by three methods: pH measurement, titration and cation - anion balance. Acceptable agreement should be sought among the three acidity results. All three methods are capable of measuring strong acids (e.g. H_2SO_4, HNO_3) which are the major concern in acid rain.

2. Titration carried out under nitrogen atmosphere using Gran's plot should be the referred titration procedure. It does not only provide uniform definition on strong acidity and weak acidity, but it allows the determination of both.

3. The theoretical correlation between pH measurement and cation - anion balance is supported by actual data when precipitation is acidic (pH<5.6), but it breaks down for basic precipitaiton (pH>5.6). The reason is not clear at present. No titration data on Alberta precipitation are available. Theoretical correlations have been established and checks should be made when data are available.

4. Precipitation acidity should be averaged on the basis of weighted hydrogen ion concentration rather than of pH values. The averaging of pH values should only be used for repetitive measurements on the same

sample lot. The precipitation acidity measured on an event basis and that measured on a bulk basis should be directly comparable by using the weighted "effective $[H^+]$" ($[H^+] - [HCO_3^-]$) average. This is supported by experimental results. Weighted $[H^+]$ average will always yield higher acidity than weighted "effective $[H^+]$" average.

5. When considering the effects of precipitation acidity on soil where chemical interactions are allowed to take place, the weighted average of "effective $[H^+]$" or $[H^+] - [HCO_3^-]$ may give a better representation on the actual acidity available.

6. Precipitation acidity expressed as $[H^+]$ and $[H^+] - [HCO_3^-]$ are interconvertible if the equilibrium CO_2 partial pressure in the atmosphere which the sample is subjected to is known.

7. Temperature effects on the acidic contribution by atmospheric CO_2 are not significant. The effects are much more pronounced with SO_2.

8. The practice of including HSO_3^- in ion analysis should be encouraged.

II. SPECIFIC CONDUCTANCE AND ION CONCENTRATIONS

1. A good linear correlation was obtained between specific conductance and ion concentrations for precipitation samples using a simple derived expression.

2. The correlation should be used as a data quality index for assessing the quality of analytical results on precipitation samples. This data quality index gives more meaningful guidelines than another index, [Cations]/[Anions] ratio.

3. Two limitations on the samples should be observed if the correlation is to be used as a quality assurance index.

   (a) the total ion concentration should not be excessively higher than normal ($\sim 10^{-3}$ equivalent per litre);

   (b) the pH should be within the range of 4 - 9.

4. No correlation was observed between concentrations of hydrogen ion and sulphate ion or nitrate ion in the precipitation samples studied.

5. Ion concentration should be expressed in terms of moles per litre or equivalents per litre rather than milligrams per litre. The preferred units enable direct comparison of species on a molecularly equivalent basis.

REFERENCES

1. American Public Health Association (APHA), American Water Works Association (AWWA) and Water Pollution Control Federation (WPCF), 1980. Standard methods for the examination of water and wastewater, 15th edition. APHA, Washington, D.C. 1134 pp.

2. Askne, C., and C. Brosset, 1972. Determination of strong acid in precipitation, lake-water and air-borne matter. Atmospheric Environment 6: 695-696.

3. Barrie, L.A. 1978. An improved model of reversible SO_2 washout by rain. Atmospheric Environment 12: 407-412.

4. Barrie L.A. 1981. The prediction of rain acidity and SO_2 scavenging in eastern North America. Atmospheric Environment 15: 31-41.

5. Barrow, G.M. 1966. Physical Chemistry, 2nd edition. McGraw-Hill Book Co., New York, 843 pp.

6. Friend J.P. 1979. A review of the atmospheric chemistry related to precipitation. Proceedings of the Advisory Workshop to Identify Research Needs on the Formation of Acid Precipitation D.H. Pack Ed., Electric Power Research Institute (EPRI) EA-1074, Special Study Project WS-78-98, pp. 2.21-2.27.

7. Galloway, J.N., G.E. Likens and E.S. Edgerton, 1976. Acid precipitation in the northeastern United States: pH and Acidity. Science 194: 722-724.

8. Gran, G. 1952. Determination of the equivalence in potentiometric titrations. Analyst 77: 661-671.

9. Granat, L. 1972. On the relationship between pH and the chemical composition of precipitation. Tellus 24(6): 550-560.

10. Hales, J. 1978. Wet removal of sulphur compounds from the atmosphere. Atmospheric Environment 12: 389-400.

11. Harned, H.S., and R. Davis, Jr. 1943. The ionization constant of carbonic acid in water and the solubility of carbon dioxide in water and aqueous salt solutions from 0 to 50°. Journal of American Chemical Society 65: 2030-2037.

12. Kluckner, P.D., and D.K. Sandberg. 1980. Project P0006, Environmental Laboratory, Ministry of Environment, Vancouver, B.C.

13. Krupa, S., and M.R. Coscio, Jr. 1976. Evaluation of a coulombic procedure for the detection of strong and weak acid components in rainwater. Journal of Air Pollution Control Association 26: 221-223.

14. Peters, R.R., H.S. Sandhu, and W.D. Hume. 1981. An analysis of precipitation in the Oil Sands area of Northern Alberat. Proceedings, Air Pollution Sessions, 15th Annual Canadian Meteorological and Oceanographic Society Conference, Saskatoon, Saskatchewan. 27-29 May 1981. pp. 147-156.

15. Reuss, J.O. 1975. Chemical/biological relationship relevant to ecological effects of acid rainfall. U.S. Environmental Protection Agency. Report EPA-660/3-75-032.

16. Tyre, S.Y., Jr. 1981. Rainwater acidity measurement problems. Atmospheric Environment 15: 57-60.

17. World Meteorological Organization (WMO). 1976. Atmospheric turbidity and precipitation chemistry data for the world 1974. Environmental Data Service, National Climatic Centre, U.S.A.

OTHER RELATED LITERATURE

1. Budiansky S. 1981. Understanding acid rain. Environmental Science and Technology 15: 623-624.

2. Ember, L.R. 1981. Acidic pollutants: hitchhikers ride the wind. Chemical and Engineering News 59(37) 20-31.

3. Hileman, B., 1981. Acid precipitation. Environmental Science and Technology 15: 1119-1124.

4. Jervis, T.R. 1979. Rainfall acidity: natural variance and subsequent time dependence of pH. Atmospheric Environment 13: 1601.

5. Kasina, S. 1980. On precipitation acidity in southwestern Poland. Atmospheric Environment 14: 1217-1221.

6. Likens, G.E. 1976. Acid precipitation. Chemical and Engineering News 54(48): 29-44.

7. Liljestrand, H.M. and J.J. Morgan. 1978. Chemical composition of acidic precipitation in Pasadena, California. Environmental Science and Technology 12: 1271-1273.

8. Lindberg S.E. 1981. The relationship between manganese and sulfate ions in rain. Atmospheric Environment 15: 1749-1753.

9. Parkhurst, W.J., R.M. Bittman and J.M. Kelly. 1980. Atmospheric wet/dry deposition: measurement and sampling variability. Proceedings of the 73rd Annual Meeting of the Air Pollution Control Association, Montreal Quebec, June 22-27, 1980.

APPENDIX I. DOCUMENTATION OF SAMPLING SITES

Sample #	Site Location	Collection Date
1	Red Deer	April 1978
2	Suffield	April 1978
3	Calgary	May 1978
4	Edmonton	May 1978
5	Red Deer	May 1978
6	Suffield	May 1978
7	Whitecourt	May 1978
8	Suffield	June 1978
9	Edmonton	February 1979
10	Calgary	June 1979
11	Edmonton	June 1979
12	Beaverlodge	July 1979
13	Calgary	July 1979
14	Beaverlodge	August 1979
15	Suffield	October 1979
16	Fort McMurray	April 1978
17	Lethbridge	April 1978
18	Rocky Mount	April 1978
19	Coronation	May 1978
20	Edson	May 1978
21	Fort McMurray	May 1978
22	Lethbridge	May 1978
23	Rocky Mount	May 1978
24	Fort McMurray	June 1978
25	Edson	July 1978
26	Edson	April 1979
27	Edson	June 1979
28	Fort McMurray	December 1979

APPENDIX II. THE COMPUTER PROGRAM FOR CALCULATIONS OF SPECIFIC CONDUCTANCE RATIO AND CATION-ANION CONCENTRATION RATIO

```
C     1982                                                YAN K. LAU                00000100
C     XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX00000200
C     CORRELATION CALCULATIONS ON DATA FROM PRECIPITATION ANALYSES                   00000300
C     ALL INPUT CONCENTRATIONS IN MG/L; SPECIFIC CONDUCTANCE IN US/CM               00000400
C     XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX00000500
C     INPUT :                                                                       00000600
C       1. 1 CARD : YEAR (I4) , E.G. 1982                                           00000700
C       2. N CARDS : ONE CARD PER DATA SET                                          00000800
C            1- 3 SEQUENCE NUMBER (I3)                                              00000900
C            6- 9 STATION ID AND MONTH SAMPLED (A4)                                 00001000
C           11-15 PH (F5.0)                                                         00001100
C           16-20 SPECIFIC CONDUCTANCE (F5.0)                                       00001200
C           21-25 SULFATE (F5.0)                                                    00001300
C           26-30 NITRATE (F5.0)                                                    00001400
C           31-35 AMMONIUM (F5.0)                                                   00001500
C           36-40 CHLORIDE (F5.0)                                                   00001600
C           41-45 SODIUM (F5.0)                                                     00001700
C           46-50 POTASSIUM (F5.0)                                                  00001800
C           51-55 CALCIUM (F5.0)                                                    00001900
C           56-60 MAGNESIUM (F5.0)                                                  00002000
C       3. 1 CARD TO TERMINATE - 0 (I5) AND DUMMIES FOR OTHER 11 PARAM.             00002100
C     XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX00002200
      DIMENSION X(500),Y(500),XX(10,500),Z(10,10)                                   00002300
C     XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX00002400
      READ(5,1) IYEAR                                                               00002500
 1    FORMAT(1I4)                                                                   00002600
      WRITE(6,111) IYEAR                                                            00002700
 111  FORMAT('0',25X,'YEAR :   ',1I4)                                               00002800
      WRITE(6,222)                                                                  00002900
      WRITE(6,333)                                                                  00003000
      WRITE(6,444)                                                                  00003100
 222  FORMAT('0  N',4X,'ST-MM',4X,'MEAS.',7X,'CALC.',8X,'KM/KC',8X,'CAT.00003200
     1/AN.',5X,'TOT. ION')                                                          00003300
 333  FORMAT(' ',16X,'CONDUCT.',4X,'CONDUCT.',5X,'(COND.',7X,'(ION',9X,'00003400
     1CONC.')                                                                       00003500
 444  FORMAT(' ',16X,'(KM)',8X,'(KC)',10X,'RATIO)',7X,'RATIO)',6X,'(MEQ.00003600
     1/L)')                                                                         00003700
C     XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX00003800
      J=0                                                                           00003900
      PX=0.0                                                                        00004000
      PXX=0.0                                                                       00004100
      PY=0.0                                                                        00004200
      PYY=0.0                                                                       00004300
C     XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX00004400
 100  READ(5,2) N,STM,PH,CON,ASO4,ANO3,BNH4,ACL,BNA,BK,BCA,BMG                      00004500
 2    FORMAT(1I3,2X,1A4,1X,10F5.0)                                                  00004600
      IF(N.EQ.0) GO TO 200                                                          00004700
      BH=10.0**(-PH)                                                                00004800
      AHCO4=(10.0**(-11.31))/BH                                                     00004900
C     XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX00005000
      XX(1,J+1)=BH*1.0E3                                                            00005100
      XX(2,J+1)=ASO4/48.0                                                           00005200
      XX(3,J+1)=ANO3/63.0                                                           00005300
      XX(4,J+1)=BNH4/18.0                                                           00005400
      XX(5,J+1)=ACL/35.5                                                            00005500
      XX(6,J+1)=BNA/23.0                                                            00005600
      XX(7,J+1)=BK/39.0                                                             00005700
      XX(8,J+1)=BCA/20.1                                                            00005800
      XX(9,J+1)=BMG/12.0                                                            00005900
C     XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX00006000
      AC=79.0*ASO4/48.0+70.6*ANO3/62.0+75.5*ACL/35.5+43.5*AHCO4*1.0E3               00006100
      BC=74.5*BNH4/18.0+50.9*BNA/23.0+74.5*BK/39.0+60.0*BCA/20.1+53.1*BM00006200
     1G/12.0+350.0*BH*1.0E3                                                         00006300
      TC=AC+BC                                                                      00006400
      AI=ASO4/48.0+ANO3/62.0+ACL/35.5+AHCO4*1.0E3                                   00006500
      BI=BNH4/18.0+BNA/23.0+BK/39.0+BCA/20.0+BMG/12.1+BH*1.0E3                      00006600
      TI=AI+BI                                                                      00006700
      R=BI/AI                                                                       00006800
      RR=CON/TC                                                                     00006900
      WRITE(6,555) N,STM,CON,TC,RR,R,TI                                             00007000
 555  FORMAT('0',I3,5X,A4,4X,F7.2,5X,F7.2,6X,F5.1,8X,F5.1,7X,F8.4)                 00007100
C     XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX00007200
```

APPENDIX II. (continued)

```
      J=J+1                                                                    00007300
      PX=PX+RR                                                                 00007400
      PXX=PXX+RR*RR                                                            00007500
      PY=PY+R                                                                  00007600
      PYY=PYY+R*R                                                              00007700
      GO TO 100                                                                00007800
C     XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX00007900
 200  VA=(PXX-PX*PX/J)/(J-1)                                                   00008000
      SCON=SQRT(VA)                                                            00008100
      VB=(PYY-PY*PY/J)/(J-1)                                                   00008200
      SION=SQRT(VB)                                                            00008300
      ACON=PX/J                                                                00008400
      AION=PY/J                                                                00008500
C     XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX00008600
      WRITE(6,666)                                                             00008700
      WRITE(6,777) J,ACON,SCON                                                 00008800
 666  FORMAT('0SPECIFIC CONDUCTANCE RATIOS, MEAS. VS CALC. :')                 00008900
 777  FORMAT('   NO. OF SAMPLES: ',I2,'   MEAN: ',F6.2,'   STD. DEV.: ',      00009000
     1F6.2)                                                                    00009100
      WRITE(6,888)                                                             00009200
      WRITE(6,999) J,AION,SION                                                 00009300
 888  FORMAT('0ION RATIOS, CATIONS VS ANIONS :')                               00009400
 999  FORMAT('   NO. OF SAMPLES: ',I2,'   MEAN: ',F6.2,'   STD. DEV.: ',      00009500
     1F6.2)                                                                    00009600
C     XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX00009700
      DO 1000 JJ=1,9                                                           00009800
      DO 2000 KK=1,9                                                           00009900
      IF(JJ.EQ.KK) Z(JJ,KK)=1.0                                                00010000
      IF(JJ.GT.KK) GO TO 2000                                                  00010100
      DO 3000 II=1,J                                                           00010200
      X(II)=XX(JJ,II)                                                          00010300
      Y(II)=XX(KK,II)                                                          00010400
 3000 CONTINUE                                                                 00010500
      CALL LSQ(J,X,Y,SLOPE,CEPT,SE,COR)                                        00010600
      Z(JJ,KK)=COR                                                             00010700
      Z(KK,JJ)=Z(JJ,KK)                                                        00010800
 2000 CONTINUE                                                                 00010900
 1000 CONTINUE                                                                 00011000
C XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX 00011100
     * WRITE(6,1100)                                                          00011200
 1100 FORMAT('1  CORRELATION TABLE : ')                                        00011300
      WRITE(6,1110)                                                            00011400
 1110 FORMAT('0',8X,'H',7X,'SO4',5X,'NO3',5X,'NH4',5X,'CL',6X,'NA',6X,'K',    00011500
     1',7X,'CA',6X,'MG')                                                       00011600
      WRITE(6,1111) (Z(1,J),J=1,9)                                             00011700
 1111 FORMAT('0H',6X,1F6.3,8F8.3)                                              00011800
      WRITE(6,1112) (Z(2,J),J=1,9)                                             00011900
 1112 FORMAT('0SO4',4X,1F6.3,8F8.3)                                            00012000
      WRITE(6,1113) (Z(3,J),J=1,9)                                             00012100
 1113 FORMAT('0NO3',4X,1F6.3,8F8.3)                                            00012200
      WRITE(6,1114) (Z(4,J),J=1,9)                                             00012300
 1114 FORMAT('0NH4',4X,1F6.3,8F8.3)                                            00012400
      WRITE(6,1115) (Z(5,J),J=1,9)                                             00012500
 1115 FORMAT('0CL',5X,1F6.3,8F8.3)                                             00012600
      WRITE(6,1116) (Z(6,J),J=1,9)                                             00012700
 1116 FORMAT('0NA',5X,1F6.3,8F8.3)                                             00012800
      WRITE(6,1117) (Z(7,J),J=1,9)                                             00012900
 1117 FORMAT('0K',6X,1F6.3,8F8.3)                                              00013000
      WRITE(6,1118) (Z(8,J),J=1,9)                                             00013100
 1118 FORMAT('0CA',5X,1F6.3,8F8.3)                                             00013200
      WRITE(6,1119) (Z(9,J),J=1,9)                                             00013300
 1119 FORMAT('0MG',5X,1F6.3,8F8.3)                                             00013400
C     XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX00013500
      STOP                                                                     00013600
      END                                                                      00013700
```

APPENDIX II. (continued)

```
C      XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX00013800
C           SUBROUTINE FOR LEAST SQUARE ANALYSIS                                       00013900
C      XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX00014000
       SUBROUTINE LSQ(N,X,Y,SLOPE,CEPT,SE,COR)                                        00014100
       DIMENSION X(500),Y(500)                                                        00014200
C      XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX00014300
       PX=0.0                                                                         00014400
       PY=0.0                                                                         00014500
       PXX=0.0                                                                        00014600
       PXY=0.0                                                                        00014700
       PYY=0.0                                                                        00014800
C      XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX00014900
       DO 200 I=1,N                                                                   00015000
       SX=PX+X(I)                                                                     00015100
       PX=SX                                                                          00015200
       SY=PY+Y(I)                                                                     00015300
       PY=SY                                                                          00015400
       SXX=PXX+X(I)*X(I)                                                              00015500
       PXX=SXX                                                                        00015600
       SXY=PXY+X(I)*Y(I)                                                              00015700
       PXY=SXY                                                                        00015800
       SYY=PYY+Y(I)*Y(I)                                                              00015900
       PYY=SYY                                                                        00016000
 200   CONTINUE                                                                       00016100
C      XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX00016200
       C=(N*SXX)-(SX*SX)                                                              00016300
       CC=(N*SYY)-(SY*SY)                                                             00016400
C      XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX00016500
       SLOPE=((N*SXY)-(SX*SY))/C                                                      00016600
       CEPT=((SXX*SY)-(SX*SXY))/C                                                     00016700
C      XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX00016800
       PR=0.0                                                                         00016900
       DO 300 I=1,N                                                                   00017000
       D=Y(I)-SLOPE*X(I)-CEPT                                                         00017100
       RR=PR+D*D                                                                      00017200
       PR=RR                                                                          00017300
 300   CONTINUE                                                                       00017400
C      XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX 00017500
       SE2=RR/(N-2)                                                                   00017600
       SE=SQRT(SE2)                                                                   00017700
       SES=SE2*(N/C)                                                                  00017800
       SEC=SE2*(SXX/C)                                                                00017900
       XS=SQRT(SES)                                                                   00018000
       XC=SQRT(SEC)                                                                   00018100
       COR=SQRT(SLOPE*SLOPE*C/CC)                                                     00018200
C      XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX00018300
       RETURN                                                                         00018400
       END                                                                            00018500
```

APPENDIX II. (continued)

INPUT

```
7879                                                                    00000100
001  R-04 7.3  32.3 3.0  2.13 1.25 0.26 0.02 0.0050.32 0.03           00000200
002  S-04 7.0  18.4 3.1  1.44 1.00 0.24 0.02 0.01 0.13 0.01           00000300
003  C-05 6.4  85.4 17.3 2.12 0.33 0.98 0.58 0.24 11.340.41           00000400
004  E-05 6.0  15.5 2.9  1.36 0.40 0.24 0.18 0.12 0.86 0.13           00000500
005  D-05 6.2  21.2 2.7  3.06 0.88 0.23 0.21 0.23 0.61 0.12           00000600
006  S-05 6.3  13.3 1.5  0.95 0.20 0.25 0.30 0.14 0.86 0.12           00000700
007  W-05 5.7  18.5 3.7  1.62 0.65 0.34 0.23 0.31 1.29 0.18           00000800
008  S-06 4.9  7.0  1.2  0.89 0.15 0.09 0.08 0.13 0.31 0.07           00000900
009  E-02 5.1  16.6 1.7  2.57 0.65 2.93 0.15 0.12 0.52 0.06           00001000
010  C-06 7.0  47.0 6.8  3.02 0.64 0.26 0.22 0.26 5.70 0.95           00001100
011  E-06 4.8  14.7 2.0  1.03 0.32 5.60 0.09 5.73 0.62 0.07           00001200
012  B-07 4.3  23.4 4.3  0.14 0.13 0.21 0.13 0.23 0.71 0.11           00001300
013  C-07 7.5  54.3 3.5  3.28 1.22 0.33 0.27 0.49 5.0  1.19           00001400
014  B-08 4.9  15.5 4.9  1.19 0.35 0.26 0.31 0.59 0.58 0.11           00001500
015  S-10 4.9  7.6  0.8  2.68 0.24 0.09 0.04 0.11 0.03 0.005          00001600
016  F-04 6.5  39.9 6.4  4.03 0.73 0.90 0.5  0.13 4.39 1.20           00001700
017  L-04 6.2  19.1 3.3  1.81 0.63 0.40 0.6  0.04 2.30 0.30           00001800
018  R-04 6.2  17.1 4.2  2.17 1.22 0.30 0.1  0.08 1.20 0.25           00001900
019  C-05 6.1  10.2 2.0  1.02 0.46 0.60 0.4  0.07 0.50 0.10           00002000
020  E-05 6.0  10.0 2.2  0.58 0.12 0.40 0.4  0.05 0.80 0.05           00002100
021  F-05 6.7  36.6 5.9  1.46 0.02 1.00 0.7  0.18 3.50 1.60           00002200
022  L-05 7.0  57.7 3.5  3.28 0.00 1.50 0.7  0.10 8.20 0.45           00002300
023  R-05 6.0  7.6  1.7  0.58 0.18 0.50 0.2  0.05 0.50 0.50           00002400
024  F-06 6.9  24.0 4.2  1.00 0.30 0.40 0.2  0.19 2.50 0.0            00002500
025  E-07 4.9  9.0  1.6  0.24 0.01 0.01 0.1  0.05 0.20 0.04           00002600
026  E-04 5.4  6.8  1.3  0.63 0.04 0.11 0.2  0.04 0.56 0.08           00002700
027  E-06 5.0  9.8  1.5  1.11 0.02 0.14 0.0  0.13 0.35 0.04           00002800
028  F-12 6.8  31.8 2.6  0.71 0.03 2.09 2.1  0.31 4.30 0.75           00002900
0    0    0    0    0    0    0    0    0    0    0    0              00003000
```

APPENDIX II. (continued)

OUTPUT

YEAR : 7879

N	ST-NM	MEAS. CONDUCT. (MI)	CALC. CONDUCT. (EC)	MM/MC (COND. RATIO)	CAT./AN. ION RATIO	TOT. ION CONC. (MEQ./L)
1	R-04	32.30	18.50	1.7	0.4	0.2909
2	S-04	18.40	14.05	1.3	0.4	0.2077
3	C-05	85.40	72.42	1.2	1.5	1.0855
4	E-05	15.50	12.82	1.2	0.9	0.1819
5	D-05	21.20	15.87	1.3	0.9	0.2248
6	S-05	13.30	9.54	1.4	1.3	0.1446
7	W-05	18.50	17.90	1.0	1.2	0.2507
8	S-06	7.00	9.89	0.7	1.2	0.0913
9	E-02	16.60	19.83	0.8	0.5	0.2446
10	C-06	47.00	42.20	1.1	1.7	0.6621
11	E-06	14.70	36.56	0.4	1.0	0.4376
12	B-07	23.40	29.10	0.8	1.2	0.2113
13	C-07	54.30	43.72	1.2	1.5	0.7305
14	B-08	15.50	19.88	0.8	0.8	0.2277
15	S-10	7.60	10.39	0.7	0.5	0.0952
16	F-04	39.90	40.61	1.0	1.6	0.6238
17	L-04	19.10	21.11	0.9	1.7	0.3195
18	R-04	17.10	20.69	0.8	1.1	0.2942
19	C-05	10.20	11.13	0.9	1.0	0.1600
20	E-05	10.00	9.78	1.0	1.0	0.1418
21	F-05	36.60	34.14	1.1	1.7	0.5428
22	L-05	57.70	43.06	1.3	2.2	0.6973
23	R-05	7.60	10.07	0.8	1.4	0.1511
24	F-06	24.00	20.15	1.2	1.0	0.3092
25	E-07	9.00	8.48	1.1	0.8	0.0700
26	E-04	6.80	7.25	0.9	1.2	0.0921
27	E-06	9.80	9.10	1.1	0.7	0.0808
28	F-12	31.80	30.45	1.0	2.4	0.5335

SPECIFIC CONDUCTANCE RATIOS, MEAS. VS CALC. :
NO. OF SAMPLES: 28 MEAN: 1.03 STD. DEV.: 0.27

ION RATIOS, CATIONS VS ANIONS :
NO. OF SAMPLES: 28 MEAN: 1.17 STD. DEV.: 0.50

CORRELATION TABLE :

	H	SO4	NO3	NH4	CL	NA	K	CA	MG
H	1.000	0.121	0.380	0.304	0.080	0.252	0.218	0.293	0.287
SO4	0.121	1.000	0.288	0.101	0.009	0.188	0.060	0.789	0.360
NO3	0.380	0.288	1.000	0.560	0.038	0.017	0.095	0.469	0.436
NH4	0.304	0.101	0.560	1.000	0.098	0.280	0.047	0.034	0.079
CL	0.080	0.009	0.038	0.098	1.000	0.225	0.822	0.114	0.053
NA	0.252	0.188	0.017	0.280	0.225	1.000	0.082	0.466	0.447
K	0.218	0.060	0.095	0.047	0.822	0.082	1.000	0.067	0.072
CA	0.293	0.789	0.469	0.034	0.114	0.466	0.067	1.000	0.551
MG	0.287	0.360	0.436	0.079	0.053	0.447	0.072	0.551	1.000

POOR

QUALITY

ORIGINAL